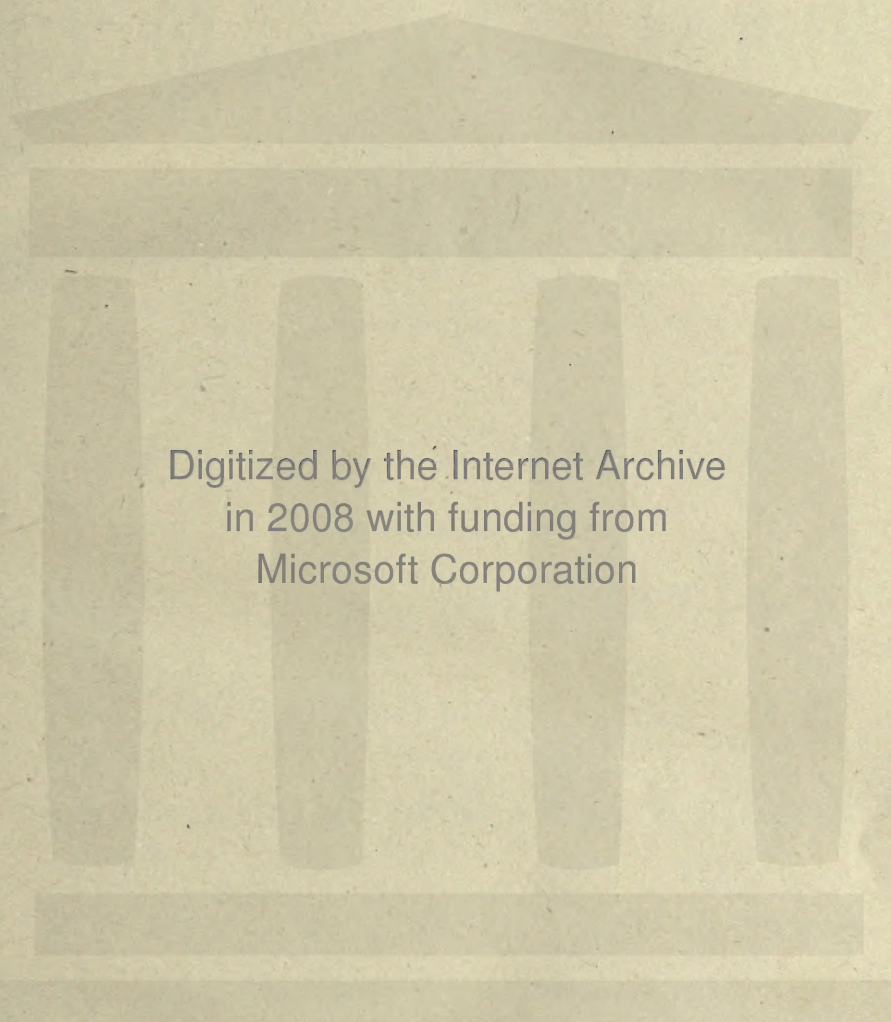




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THE CHEMICAL NEWS, JULY 13, 1900.

THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXXI.—1900.

51566
1901

LONDON:

PUBLISHED AT THE OFFICE, 6 & 7, CREED LANE, LUDGATE HILL, E.C.
AND SOLD BY ALL BOOKSELLERS.

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No. 2093.—JANUARY 5, 1900.

THE RELATION BETWEEN BOILING-POINT AND MELTING-POINT IN THE HYDROCARBONS.

By THOMAS BAYLEY, Assoc.R.C.Sc.

THE accompanying table shows the melting- and boiling-points of the hydrocarbons of the paraffin, olefine, and acetylene series in absolute degrees centigrade.

The melting-point and the boiling-point *in vacuo* are points that mark two important changes in the condition of a body under the influence of heat. The melting point is the temperature at which the internal attractions conditioning solidity are overcome. The boiling-point *in vacuo* is the temperature at which disappear the internal attractions which have, between the melting-point and the boiling-point, preserved the substance in the liquid form. There are, of course, no determinations of boiling-point made in an absolute vacuum, but some of the data in the table are for a pressure of 15 m.m., at which the external force of atmospheric pressure is reduced to an insignificant amount.

According to the usual definition, the boiling-point of a substance is the temperature at which the pressure of its vapour is equal to the pressure of the surrounding atmosphere, and since probably every substance has a vapour pressure, however small, at and below the melting-point, it would seem to follow that every liquid must boil at any temperature in an absolute vacuum if we neglect such considerations as the cohesion between the substance and the walls of the vessel, the pressure of the liquid column, &c., &c.

According to this view, the term, boiling-point *in vacuo*, has no definite meaning. At the same time the term has a very definite meaning at those low pressures which are the nearest approach to true vacua possible in ordinary chemical investigation.

If we plot the boiling-points of a liquid under various pressures the curve indicates that *in such ordinary vacua* the relations between the increment of vapour pressure and the increment of temperature undergo an abrupt change at or near the boiling-point *in vacuo* (meaning by this a very low pressure). Below this boiling-point the increment of vapour pressure is relatively small, and the heat entering the liquid is for the most part expended in raising the temperature. At this boiling-point the internal attractions having given way before the intensity of thermal vibration, the added heat no longer causes rise of temperature, but wholly passes into the latent form.

If now we suppose a liquid *in absolute vacuo* (supposed to be permanently maintained) to be placed near a source of heat, then, according to the view previously stated, it will boil at any temperature, because at that temperature it has a vapour pressure. But while the heat is passing into the substance at temperatures near to the melting-point, the thermal energy for the most part expends itself in increasing the thermal vibrations of the particles of the substance (*i.e.*, the temperature), but the ratio between

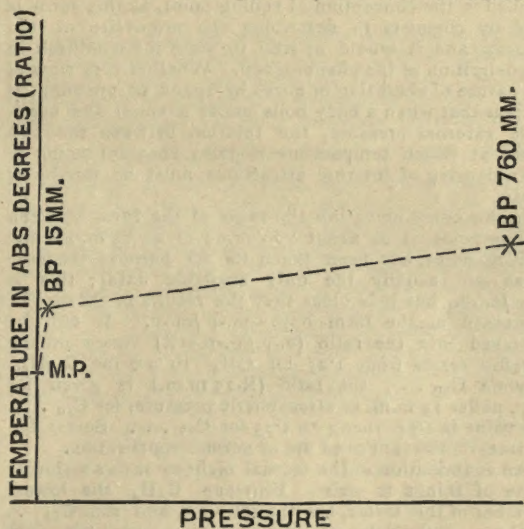


DIAGRAM SHOWING TWO POINTS ON THE CURVE OF
BOILING-POINTS AT VARIOUS PRESSURES FOR $C_{19}H_{40}$
AND $C_{20}H_{42}$.

the heat so engaged and the heat rendered latent in forming vapour tends constantly to decrease, through increase of the lower term, until at length ebullition occurs at a temperature *no longer tending to rise*. This temperature may be called the "intrinsic boiling-point" of the substance. When heat is imparted to a solid, having a vapour pressure, a similar ratio exists and similarly tends to diminish, and the only difference between the two cases is that in the one case the vapour is evolved at the surface of the body (sublimation), and in the other is formed in bubbles at the region where the

Paraffins.				Olefines (normal).					
	M.-p.	B.-p.	Ratio: B.-p./M.-p. 760 m.m.	Ratio: B.-p./M.-p. 15 m.m.		M.-p.	B.-p.	Ratio: B.-p./M.-p. 760 m.m.	Ratio: B.-p./M.-p. 15 m.m.
CH ₄	87	109	1'25		C ₂ H ₄	113	170	1'5	
C ₂ H ₆			(1'5)?						
C ₅ H ₁₂ (tert.)	253	282	1'11						
Normal Hydrocarbons—									
C ₉ H ₂₀	222	423	1'9						
C ₁₀ H ₂₂	241	446	1'85						
C ₁₁ H ₂₄	247	468	1'9						
C ₁₂ H ₂₆	261	487	1'88		C ₁₂ H ₂₄	242	369†		1'52
C ₁₃ H ₂₈	267	507	1'9		C ₁₄ H ₂₈	261	400†		1'53
C ₁₄ H ₃₀	278	526	1'9		C ₁₆ H ₃₂	277	{ 547 428†	1'98	1'54
C ₁₅ H ₃₂	283	544	1'9		C ₁₈ H ₃₆	291	452†		1'55
C ₁₆ H ₃₄	291	561	1'9						
C ₁₇ H ₃₆	296	576	1'95						
C ₁₈ H ₃₈	301	590	1'96						
C ₁₉ H ₄₀	305	603	2'0						
C ₂₀ H ₄₂	310	478*		1'54					
C ₂₁ H ₄₄	313	488*		1'57					
C ₂₂ H ₄₆	317	498*		1'57	C ₁₂ H ₂₂	264	378†		1'44
C ₂₃ H ₄₈	321	507*		1'55	C ₁₄ H ₂₆	279	407†		1'46
C ₂₄ H ₅₀	324	516*		1'53					
C ₂₇ H ₅₆	333	543*		1'63					
C ₃₁ H ₆₄	341	575*		1'68	C ₁₆ H ₃₀	293	433†		1'47
C ₃₂ H ₆₆	343	583*		1'70	C ₁₈ H ₃₄	303	457†		1'50
C ₃₅ H ₇₂	348	604*		1'73					

* Beyond C₂₀H₄₀ the determinations of boiling-point are made at 15 m.m. pressure owing to the instability of the hydrocarbons at high temperatures and pressures.

† Boiling-point under 15 m.m. pressure.

heat gains access to the liquid. The idea of fixity is implied in the conception of boiling-point, as this term is used by chemists in describing the properties of substances, and it would be well to state the condition in the definition of the phenomenon. Whether this view of the nature of ebullition *in vacuo* be sound or unsound, it is clear that when a body boils under a small and negligible external pressure, the relation between the two crises at which temperature remains constant owing to the unloosening of internal attractions must be worthy of study.

In this communication the value of the ratio between boiling-point at or about 760 m.m. or at 15 m.m., and melting-point, has been taken for the purpose (because these are usually the only available data); this is b.-p./m.-p., but it is clear that the results might also be expressed in the form b.-p.—m.-p./m.-p. It will be observed that the ratio (b.-p./m.-p.=R) varies in the paraffin series from 1'25 for CH₄, to 2'0 for C₁₉H₄₀. Beyond C₁₉ . . . the ratio (R-15 m.m.) is given for b.-p. under 15 m.m. of atmospheric pressure, for C₂₀ . . . the value is 1'54, rising to 1'73 for C₃₅ . . . So far the hydrocarbons mentioned are of normal constitution.

An examination of the normal olefines shows a similar state of things to exist. Ethylene, C₂H₄, the lowest member of this series, has the ratio 1'5, and from C₁₂ . . . to C₁₈ . . . the value of R-15 m.m. rises very little, only from 1'52 to 1'55. The variation from C₉ . . . to C₁₉ in the normal paraffin series is only from 1'9 to 2'0. The ratio R for the middle portions of both series is therefore almost constant, with a tendency to increase with the increasing length and consequent decreasing stability of the chain. It is apparent that the rational values are approximately equal for corresponding members of the two series, since Meyer Wilderman (*Ber.*, xxiii., 1254) has shown that in organic series the ratio—

Boiling-point at small pressure

Boiling-point at 760 m.m.

is a constant. It is probable that the ratio for C₂H₆, which is not known, is 1'5 (= R for C₂H₄).

Marsh gas (CH₄), which is the most stable member of the paraffins, not being decomposed at a low red heat, has the ratio 1'25; from this to the two carbon chain in C₂H₄ the rise is rapid, viz., to 1'5. As is well known, both melting-point and boiling-point in these compounds increase with lengthening chain, the values of R indicate that boiling-point rises relatively more than melting-point.

The (normal) paraffins afford an example of a series of compounds formed by the consecutive addition of a common constituent, the group CH₂. The value of R in this series is 1'25 for the lowest member, and at the middle of the series it is almost equal for neighbouring members, but a little higher for the greater molecule. The ratio for H₂, the lowest member of group I., is 1'25 (from Dewar's results), and in the middle of the series Na and K have a rational value of 2'75 and 2'80 (Perman's data). The parallel is interesting.

The tertiary paraffin C₅H₁₂, with a symmetrical molecule containing a central carbon atom directly united to four others, has the low rational value 1'11. Here, linkage of carbon to carbon causes the melting-point to be relatively high and the boiling-point to be relatively low. The hydrocarbon benzene, C₆H₆, in which the carbon chain has no ends, but is closed, and the molecule can therefore exhibit symmetry about three lines drawn through its carbon atoms and the centre of the hexagon (plane formula), has R = 1'26. Here there is no side chaining to explain the low value, but there is linkage of carbon to carbon to a greater or less extent, according to the various conceptions of the nature of the benzene ring. Kekulé's formula shows only bonding of each carbon atom to two others, with alternate double and single linkage. But this arrangement in the olefines does not co-exist with low ratio. There are several other formulæ for benzene; that of Claus and Körner and that of Ladenburg indicate a linkage of each carbon atom to three others; in Dewar's formula two of the six carbon atoms are triply united by a *para* bonding.

Just as the value of R rises from 1'25 in CH₄ to 1'5 in C₂H₄, so it is raised by the union of two rings in diphenyl from 1'26 to 1'54 (difference = 0'27).

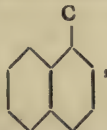
Where the two rings, as it were, partially coalesce in naphthalene, $R = 1.40$, which is the mean between 1.26 and 1.54. For the highly symmetrical triple ring of anthracene, with high linkage of carbon to carbon, and a central *para* bonding, the ratio is 1.28, while it is 1.63 for the isomeric but less symmetrical phenanthrene which has no *para* bonding. The effect of symmetry upon the rational value is illustrated by a study of the methylbenzenes. $C_6H_5CH_3$ has $R > 1.5$. For the xylenes $C_6H_4(CH_3)_2$, the value of R is 1.42 for the symmetrical (*para*) isomer and 1.69 for the *o*-compound (difference = 0.27). In symmetrical tetra-methyl benzene (1:2:4:5) (durene) the ratio is 1.31, in iso-durene (1:3:4:5) it is 1.31, and it is 1.77 in the one-sided (vicinal) prehnitene. When the nucleus is completely encircled with six methyls in hexamethyl benzene R is 1.23, but in penta-methyl benzene, with a gap in the sentinel methyl groups, the ratio is 1.55. The ethyl-benzenes are analogous as regards the value of R , but the values are individually greater owing to the effect of the longer side chains. In methyl diphenyl (1:3)—



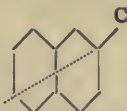
R is > 2.1 ; in the *para* isomer,—



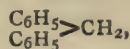
it is 1.98. Again, (a) methyl naphthalene,—



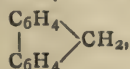
has $R > 2$; but the (β) isomer, which has a kind of symmetry, thus—



exhibits the lower ratio 1.68. In symmetrical diphenyl-ethylene R is 1.46, it is much higher in the unsymmetrical isomer. The ratio for symmetrical diphenylethane is 1.69, it is greater for the unsymmetrical isomer; the symmetrical and unsymmetrical diphenyl ethylenes have a similar relationship. *Para* diphenyl benzene has the ratio $R = 1.40$, its isomer shows c 1.80. The effect of dissolving the *para* linkage is shown in the hydrogenising of anthracene. R for anthracene is 1.28, for the dihydride it is 1.54 (difference = 0.26). These two hydrogens are taken on at the expense of the *para* linkage. The further addition of four hydrogen atoms in the hexahydride raises the value of R to 1.67, *i.e.*, only by half as much, *viz.*, 0.13. The change from naphthalene to the dihydride is from 1.40 to 1.68, the difference being 0.28. The comparison of the values of R in diphenyl methane,



and diphenylene methane (fluorene),—



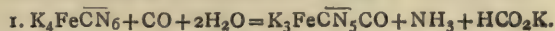
is interesting. The value of R in the former is 1.799, and in the latter 1.49, and the difference is 0.31 (the boiling-points are stated approximately). Here, assuming 0.065 for the increase in R caused by the two additional hydrogen atoms (*i.e.*, the values indicated by anthracene hexahydride) added to the rings, we obtain a value of about 0.25 for the direct linkage between the rings, which

is very near the value of the linkage difference between CH_4 and C_2H_4 (0.25) and between benzene and diphenyl (0.27). The values of R for acenaphthene, $C_{10}H_6, C_2H_4$, and for acenaphthylene, $C_{10}H_6, C_2H_2$, are the same, *viz.*, 1.48. Here the two hydrogen atoms are added to the fatty chain at the expense of a double bond, and we have seen in the paraffins and olefines that no appreciable difference of rational value exists between corresponding members of these series. Taking the rational values quoted previously, at least eleven pairs of compounds can be found with differences varying from 0.26 to 0.29 (mean 0.278), while seven pairs exhibit a difference ranging from 0.12 to 0.14 (mean 0.13), and six pairs have a difference varying from 0.41 to 0.43 (mean 0.423). It must be remembered that many of the boiling-points used in the computation of the values of R in this communication are made at various pressures in the neighbourhood only of the normal pressure and at pressures frequently not stated. To the uncertainty arising in this way must of course be added that due to errors in the melting-point determinations. But as far as one can judge from the available data, limited owing to the non-existence of both melting-point and boiling-point determinations for the same compound, it would appear that the study of the ratio between melting-point and boiling-point in the hydrocarbon series throws fresh light upon the connection between molecular constitution and these physical properties of substances. In this communication an attempt has been made to discover the nature of the connection.

ON THE THEORY OF THE ACTION OF CARBONIC OXIDE ON DISSOLVED FERRO-CYANIDE OF POTASSIUM.

By J. A. MULLER.

On heating a solution of the yellow prussiate of potash in an atmosphere of carbonic oxide, I have already shown (*Comptes Rendus*, vol. lxxvii., p. 123), that a carbonyl-ferrocyanide of potassium is formed, and further, I proved that the reaction takes place according to the equation—



However, by working under better conditions of temperature, &c. (130—135°), the coefficient of the reaction hardly exceeds 0.9, or 90 per cent, even when using a quantity of carbonic oxide slightly in excess of the amount required theoretically. If the proportion of carbonic oxide is increased the coefficient of the reaction increases. Thus, by heating for forty-eight or fifty hours to 130—135° in a Wiesnegg apparatus, fitted with an Arsonval regulator, a practically constant volume of carbonic oxide in the presence of decreasing quantities of dissolved prussiate, I obtained the following results:—

Proportion of CO_2 per molecule of prussiate.	Coefficient of the reaction.
1.3	0.91
1.7	0.96
3.2	0.98

The increase of the coefficient of the reaction with the proportion of carbonic oxide used might cause us to believe that this reaction is limited by the inverse reaction; this, however, is not the case, or at least if there is any inverse reaction, it plays only a secondary part in the limitation. This is proved by the following experiments:

A mixture composed of—

K_3FeCN_5CO		1.576 grms.
NH_3		0.081 "
HCO_2K		0.400 "
Water..		10 c.c.

is heated for fifty hours at 130—135° in an atmosphere of

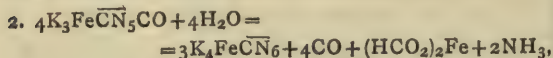
nitrogen; thus, the mixture contains the first three compounds in the proportion of the inverse reaction of equation (1). On opening the tube, I found that the quantity of ammonia had remained the same, but that nevertheless a quantity of ferrocyanide of potassium, equal to 0.101 grm., had been formed, while the greater part of the carbonylferrocyanide, that is to say, 1.418 grms., had not undergone any decomposition.

In a second experiment, a solution of 1.576 grms. of pure carbonylferrocyanide of potassium in 10 c.c. of water was heated under the same conditions, that is to say, for fifty hours, to 130–135° in an atmosphere of nitrogen. The gaseous volume of the tube was equal to 79.5 c.c. at 25° and 756 m.m. pressure. On opening the tube, I first observed that this gas, in the dry state, was composed as follows:—

Carbonic oxide	6.7
Nitrogen (by difference)	93.3
	100.0

As to the liquid, it held in suspension, as also did that in the previous experiment, a very slight greenish white precipitate containing iron. It consisted of 0.072 grm. of ordinary prussiate and 0.0028 grm. of ammonia; finally, there remained 1.459 grms. of carbonylferrocyanide of potassium unchanged.

Admitting that the prussiate found in this last experiment is formed according to the following equation—



there should be formed 0.0073 grm. of carbonic oxide (found 0.0059 grm.), and 0.0022 grm. of ammonia (found 0.0028 grm.). Considering the small quantities of the different compounds used, these figures may be looked upon as sufficiently concordant for us to infer that the ferrocyanide of potassium found in this experiment is actually formed according to the equation (2), and that it is entirely, or at any rate principally, this reaction that limits reaction (1) in the preparation of carbonylferrocyanide of potassium.

If, in the preceding experiment we replace the atmosphere of nitrogen by an atmosphere of carbonic oxide, the quantity of carbonylferrocyanide which is decomposed is almost nil (0.32 per cent). Under these conditions, therefore, the reaction (2) does not take place. The result is that by heating a solution of prussiate in the presence of a sufficient excess of carbonic oxide this prussiate should be practically entirely changed into carbonylferrocyanide; it is this that the direct experiments mentioned at the commencement of this paper have already shown.

The last experiment with which we have to deal proves that the resistance of carbonylferrocyanide of potassium to direct hydrolysis is greater, even much greater, at 130–135° than that of ferrocyanide of potassium. In fact, on heating 30 c.c. of a solution of prussiate, at 200 grms. of crystallised salt per litre, for forty-eight hours at 130–135° (the gaseous volume of the tube was then only 8 c.c., and was filled with air), there is formed 0.1380 grm. of formate of potassium, and 0.0284 grm. of ammonia. Both these compounds arise from the hydrolysis of 0.1075 grm. of CNK, which would give theoretically 0.1388 grm. of HCO_2K , and 0.0282 grm. of NH_3 . During the heating, there is also formed a greenish-yellow precipitate weighing, when dry, 0.1013 grm., and appearing to consist of a complex cyanide of iron and potassium.*

It is thus, to the slight stability of the dissolved ferrocyanide, compared with that of the carbonylferrocyanide, in the presence of an excess of carbonic oxide, and at a temperature not exceeding 130–135°, that we are led to

attribute the formation of this latter to the detriment of the former; in the presence of water a group, CNK, of the molecule of prussiate, is hydrolysed; this group, CNK, is then immediately substituted by a molecule of oxide of carbon with the formation of carbonylferrocyanide of potassium.

In all cases the presence of free carbonic oxide is necessary for the formation of this salt. I have made a considerable number of experiments in which carbonylferrocyanide ought theoretically to have been formed, without ever finding a trace of this compound when the mixture was not in the presence of carbonic oxide. On the other hand, water is no less indispensable to the reaction. In fact, by heating dry finely powdered ferrocyanide of potassium for fifty hours at 127–136°, spread in a thin layer in a sealed tube containing dry carbonic oxide (1.1 molecule), there is not a trace of carbonylferrocyanide of potassium formed.—*Bull. Soc. Chim.*, Series 3, vol. xli., No. 10.

FLUORINE IN THE MINERAL WATERS OF SPAIN AND PORTUGAL.

By A. J. FERREIRA DA SILVA and ALBERTO D'AGUIAR.

UNDER this title we published, on the 1st of May this year (1899), in a Portuguese medical journal (*A Medicina Moderna*, May, 1899, p. 280–281), a preliminary note which we think is worth reproducing here with a few additions and corrections, as it appears to us to throw some light on the issue raised in the *Comptes Rendus* of the same date, by M. F. Parmentier (*Comptes Rendus*, No. 18, May 1, 1899, p. 1100–1101), in his paper, "On the Fluorine supposed to be contained in certain Mineral Waters." The following is what we then wrote:—

"Fluorine was first detected and estimated by Berzelius in the celebrated Karlsbad waters; other chemists found it later on in several different springs; the work of Nicklès on the fluorine in the waters of Plombières may be specially mentioned.

"It is, however, certain that, according to all published analyses, fluorine occurs only in traces, or in very small quantities.

"Among our own mineral waters, that of Gerez is remarkable for the quantity of this element present according to the analysis of M. Souza Reis (1885). M. Ricardo Jorge, who has examined these waters in a most searching manner, classifies them as being the most fluorised waters in Europe, and he remarks that the water from Gerez contains four times as much fluorine as that from Karlsbad (Richardo Jorge, *Caldas do Gerez, O Gerez Thermal*; Porto, 1891, p. 52).

"The illustrious professor has not only tabulated, from this point of view, the values of the other similar springs in Europe as compared with that of Gerez, but he has also shown by experimental research ("Trabalhas experimentaes e clinicas sobre as fluoretos alkalinos"; *Caldas do Gerez*; Porto, 1888), the therapeutic action of the alkaline fluorides; and he has thus cleared up the mystery which enveloped the salutary action of these waters.

"One of us, being engaged in the analysis of the spring at Campilho at Vidago, found in this water the presence of fluorine in much greater quantity than it had been found in other springs from the northern part of Portugal; and we were even able to estimate it, an estimation which we hope to repeat by means of a new and more precise method.

"The following are the quantities of fluorine found in the two waters:—

Fluorised Portuguese Waters.

Gerez (fluoride of sodium)	0.022880 grm.
Vidago (Campilho spring) fluoride, of sodium	0.000942 "

* When treated with fuming hydrochloric acid, a part of this precipitate is dissolved; on then diluting the mixture with water a fairly abundant precipitate of prussian blue is formed.

"In Spain the question of the existence of fluorine in mineral waters was examined by Dr. Joseph Casares Gil, ten years after the work done in Portugal, in a memoir presented to the Royal Academy of Arts and Science at Barcelona, and in a note dated April 16, 1896, and published in the *Boletín* of the same academy in the month of April, 1898, pp. 420-424.

"On analysing two samples of sulphurous waters, the one hot and the other cold, from the province of Lugo, in the town of the same name, at Guitiriz, Dr. Casares Gil found the following results:—

Spanish Fluorised Waters.

Lugo (fluoride of sodium)	0.0242 grm.
Guitiriz (fluoride of sodium)	0.0234 "

"The same chemist was of the opinion, and with good reason, that the proportion of fluorine in these two samples being so considerable, this fluorine might be detected without having recourse, as is usual, to the evaporation of several litres; and for this purpose he devised an apparatus by which the presence of fluorine is detected by the transformation of the fluoride of silicon, which can be made to contain the whole of fluorine in the water, into gelatinous silica,* he was able to obtain a very distinct silica ring when working on only 500 c.c. of these waters.

"The author quoted asserts that fluorine is to be found in many mineral waters in much higher proportions than has been observed up to the present, and that for this reason many analyses should be revised; it can be safely affirmed that fluorine is present in noticeable quantities in many alkaline and sulphurous springs in Galicia (Verin, Molgas, Burgas de Orense, Carbalho, Carballino, Caldeas de Fuy), Caldas de Reyes, Catoira, and Contrexville in France.

"How does it happen that up to the present time the presence of fluorine in these waters has never been detected?

"The author replies that very often it has not been tested for, because its presence was considered to be so rare and of such little interest; on other occasions it has not been detected on account of the inexact methods of detection which, through a typographical error in the older editions of Fresenius's "Qualitative Analysis," both in German and in the French translations, recommended the detection of fluorine by the corrosion of glass by the hydrofluoric acid, given off when the residue from the evaporation of the water (after treatment with water and precipitation by chloride of lime) was treated with sulphuric acid.

"It is, however, certain that with mineral waters containing silica and silicates, the precipitate of fluoride of calcium is found to be associated with silicate of lime, and in the treatment with concentrated sulphuric acid it is not usually hydrofluoric acid that is given off, although fluorides may, all the same, be present in the water, but fluoride of silicon, the action of which on glass is barely noticeable. In the case of siliceous waters the glass-corrosion test by hydrofluoric acid should not be used for testing for fluorine, but the transformation into fluoride of silicon.†

"The existence of fluorine in mineral waters brings up a certain number of analytical questions.

"One of these is, the exact determination of the silica in the presence of fluorine. The other is, the loss of fluorine and silica, in the form of fluoride of silica, which should take place when the sulphated residue of the

waters is determined as a check on the analysis, from which it results that the residue found might be less than that calculated, although the analysis may have been conducted with the utmost care.

"It seemed to us to be of interest to verify the presence of the silica ring according to Dr. Casares Gil's method in the Portuguese fluorised waters, and in those of Caldas da Saude (at Santo Thyrsó), recently analysed by one of us.

"We verified the accuracy and the sensitiveness of the process, and, that of the three Portuguese mineral waters, those of Gerez gave a perceptible reaction with only 250 c.c., and those of Campilho with 500 c.c.

"In the same quantities, fluorine was not detected in the waters of Caldas da Saude.

"We propose carrying on this research on mineral hydrology, which appears to be of great interest."—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 20—21.

ON THE

ANALYSIS OF VULCANISED INDIARUBBER.

By CARL OTTO WEBER.

THE method I proposed some time ago (*Chemiker Zeitung*, 1894, 1696) for separating indiarubber from the mineral matter it contains, a method which consists in boiling the finely divided rubber in a flask fitted with a vertical condenser with nitrobenzene, has given in practice very satisfactory results. The only drawback to this method is the difficulty sometimes experienced in eliminating the mineral matter from the solution of the products of decomposition of the indiarubber.

In most cases this inconvenience can be guarded against by diluting the solution with a large quantity of ether. If we have to deal with African rubbers, the quantities of ether to be used are relatively very large. Further, the treatment with nitrobenzene gives rise to a phenomenon that I have only recently observed for the first time.

While analysing a sample of rubber (a) by the viscous decomposition method, and another sample (b) made in the same manner and of irreproachable quality, I obtained the following results:—

	a.	b.
	Per cent.	Per cent.
Oily extract	8.35	2.82
Indiarubber	9.85	12.73
Inorganic matter	79.9 { 63.11 min. 16.79 carb.	82.34 { 62.81 min. 19.53 carb.
Sulphur (total)	1.89	2.10

The presence of such considerable quantities of carbon or carbonaceous material, on the one hand, and the incredibly small proportion of rubber in the product, on the other hand, has caused some apprehension as to the correctness of this analysis, and further examination has only strengthened this doubt.

Under ordinary conditions the figures representing "oily extract" would be attributed to the rubber from which this extract was made, seeing that, as far as the manufacturer is concerned, the extract forms a part of the rubber itself. But in these two samples the quantity of extract is nearly triple the amount that it is in ordinary indiarubber. Although the proportion of extract varies considerably with the kind of rubber, still, so pronounced a difference as that observed between the samples a and b appears to be hardly credible. Further, in the samples analysed, the increase in the quantity of extract found is counteracted by the diminution of the amount of rubber found, which seems to indicate that the oily extract is for the most part only a product of decomposition of the indiarubber. The analysis also shows that the proportions of carbon follow the proportions of rubber present. All these facts tend to show that the carbon found did not pre-exist in the product, but results from the action of

* Dr. Casares Gil describes his apparatus in a note sent to M. R. Fresenius, and published in the *Zeit. für analytische Chemie*, vol. xxiv., p. 546.

† The error to which M. Casares Gil makes allusion is still found in the 7th French edition of 1885 ("Traité d'Analyse Qualitative," de R. Fresenius, p. 386), where we find quoted the reaction 146.5 of page 241, when it should have been 146.6. In the 8th edition of 1896 (pp. 254 and 429), and in the 9th edition of 1897 (pp. 302 and 494) the error has been corrected.

the boiling nitrobenzene on the indiarubber. It is also possible that its formation is due to the action of the high temperature at which nitrobenzene boils.

I endeavoured to dissolve the samples in question in nitrobenzene at a temperature of 170–190°, but the attempts were fruitless. Either the solution was incomplete, or else the carbon made its appearance in the same proportion as in the analysis quoted above.

Starting from the idea that the preliminary swelling of the rubber in chloroform might facilitate its disaggregation by the boiling nitrobenzene, I placed 3 grms. of each sample into the wide-necked flasks used for the treatment with nitrobenzene; I then added 3 c.c. of chloroform to each, corked the flasks, and allowed them to stand for about an hour. At the end of this time the indiarubber was enormously swollen. Without driving off the chloroform I added to each flask 50 c.c. of nitrobenzene, fitted a vertical condenser to each flask, and heated to boiling in a paraffin bath. At the end of an hour the reaction was stopped, and after cooling, 100 c.c. of ether were added to each flask, and the contents then filtered. The results obtained were as follows:—

	a. Per cent.	b. Per cent.
Inorganic material.. ..	63·33	63·02

There was not a trace of carbon present. From these results it appears that the previous swelling of the rubber by means of chloroform has the effect of totally preventing carbonisation. The favourable action exercised by the chloroform in the process is beyond doubt; but it must not be forgotten that the addition of chloroform to the nitrobenzene considerably lowers the boiling-point of the latter. A direct experiment has shown that a mixture of chloroform and nitrobenzene in the proportions mentioned above boils at a temperature of from 170 to 180°. It is to the action of the chloroform on the rubber at this temperature that I attribute the energetic disaggregation of the latter.

The experiment described above appears also to show that the carbonisation of the rubber by boiling nitrobenzene was principally due to the influence of the high temperature, which influence was probably seconded by the oxidising action of the nitrobenzene. But the exact analysis of the organic matters obtained in the two series of analyses has shown where to look for the true cause of the carbonisation of the rubber.

Treatment by Nitrobenzene only.

	a. Per cent.	b. Per cent.
Carbonaceous matter	17·22	19·93
Mineral matter—		
CaCO ₃	20·78	21·04
PbCO ₃ }	40·27	41·83
PbO }		
PbS }	2·10	1·00
PbSO ₄ }		
Total mineral matter	63·15	63·87

Treatment by the Mixture of Chloroform and Nitrobenzene.

	a. Per cent.	b. Per cent.
Carbonaceous matter	traces	traces
Mineral matter—		
CaCO ₃	21·02	21·11
PbCO ₃ }	32·22	31·56
PbO }		
PbO ₂ }	9·97	10·05
PbS }	1·05	0·88
PbSO ₄ }		
Total mineral matter	64·26	63·60

It is noticeable that the mineral matter isolated in treating the rubber with the mixture of chloroform and

nitrobenzene contains a considerable quantity of peroxide of lead, while at the same time it is almost completely free from carbon. On the contrary, the treatment of rubber with nitrobenzene at once gives a large proportion of carbon and hardly any peroxide of lead. It is thus beyond doubt that at the temperature of boiling nitrobenzene (208°) the peroxide of lead contained in the rubber attacks the latter with the formation of carbon, a reaction which, at the temperature of the boiling mixture of chloroform and nitrobenzene, does not evidently take place. It is hardly probable that the peroxide of lead found exists as such in the inorganic residue.

It seems, moreover, certain that it comes from the minium during the treatment of the residue by dilute nitric acid. Minium is often used in the manufacture of vulcanised articles by heat; above all, if a soft rubber is used. In such a case the minium exercises a hardening action, that is to say, slightly oxidising (?). By calculating the peroxide of lead found in the second analysis as minium, the composition of the inorganic residue should be expressed by the following figures:—

	a. Per cent.	b. Per cent.
CaCO ₃	21·02	21·11
PbCO ₃ }	22·92	22·19
PbO }		
Pb ₂ O ₃ }	19·27	19·42
PbS }	1·05	0·88
PbSO ₄ }		
	64·26	63·60

These figures show that the rubber used contained almost equal quantities of carbonate of lime, carbonate of lead, and minium.

From the purely chemical point of view, the question of deciding what transformation is undergone by the rubber under the action of the treatment with nitrobenzene alone, or in the presence of chloroform, is one of great interest; but up to the present I have not had an opportunity of studying this question. As I have already stated, the indiarubber does not exist as such when in nitrobenzene solution. It must therefore be, that the treatment has the result of degrading the molecule of indiarubber.

Now, we know that when submitted to dry distillation rubber is transformed almost quantitatively into hemiterpene, dipentene, and polyterpenes. We might therefore suppose that vulcanised rubber would undergo an analogous decomposition when treated with boiling nitrobenzene. To this it might be objected that non-vulcanised rubber becomes quite viscous at the temperature of boiling nitrobenzene, without giving any products of distillation, while vulcanised rubber is hardly changed at this temperature.

But still it is always the fact that indiarubber commences to decompose, though slowly, in the neighbourhood of 200°. It is again very probable, considering the nature of the products of decomposition of indiarubber, that isoprene, which constitutes about 15 per cent of the portion distilled, is not an immediate product of the decomposition of rubber, and that there are first formed bodies of a high molecular weight (polyterpenes?), which then give birth to citrene and isoprene. This view seems to be confirmed by the fact that I have often noticed in the dry distillation of different kinds of rubber, that the slower the distillation, and therefore the lower the temperature, the lower is the return of citrene and isoprene. The best results are obtained by introducing small portions of rubber at a time into a retort heated to redness. From these facts I think I may conclude that, under the influence of a high temperature, indiarubber does not decompose into small molecules, but first gives rise to products of a high molecular weight.

Further, in the treatment of indiarubber by nitrobenzene—that is to say, at a relatively low temperature—rubber ought to give products of a high molecular weight,

perhaps even one single product. If such is the case, we should be able not only to estimate rubber directly in manufactured articles, but, further, we should by so doing be making an important step forward towards a knowledge of the nature and the size of the molecule of india-rubber. I am continuing the experiments I have started in this direction.—*Zeitschrift für angewandte Chemie*, 1898, p. 313.

THE ACTION OF ACETYLENE ON THE OXIDES OF COPPER.*

By F. A. GOOCH and DEFOREST BALDWIN.

In a recent paper by Erdmann and Köthner (*Zeitschr. für Anorg. Chem.*, xviii., 49) an account is given of the formation of a peculiar, light brown, highly voluminous substance by the action of acetylene below 250° C. upon cuprous oxide, or even (though more slowly) upon copper. The product obtained by passing acetylene during eighteen hours over 1 grm. of cuprous oxide (prepared from copper sulphate, grape sugar, and sodium hydroxide) amounted to 7 grms., and filled a space of nearly 300 c.m.³. At higher temperatures a black carbonaceous mass is the result, and at red heat (400–500° C.) carbon is deposited in graphitic condition. The light brown fluffy material yielded cuprous chloride to hydrochloric acid, a distillate from its mixture with zinc dust possessing the characteristic of naphthene, or, at higher temperature and under rapid heating, aromatic compounds among which naphthalene and a kresol were indicated. Erdmann and Köthner classify this body as a very complex but non-explosive copper acetylene (acetylen-kupfer), and from their analyses deduce the formula $C_{44}H_{64}Cu_3$. Apart from the unusual constitution of this symbol, its most striking peculiarity is that it implies a loss of carbon, rather than hydrogen, from the acetylene in the reaction with cuprous oxide—a condition of affairs which would be most remarkable in the light of Campbell's experience (*Amer. Chem. Journ.*, xvii., 690), according to which acetylene, passed over palladinised copper oxide, yielded water at 225–230°, and carbon dioxide only when the temperature rose to 315–320° with the formation of a black deposit. Upon scrutinising the figures of Erdmann and Köthner with care, however, it appears that the formula given by these investigators rests upon some oversight in calculation: the ratio of carbon atoms to hydrogen atoms proves to be actually, according to the data given, 6.45 : 5.70; which means, of course, that the new product is deficient, as would be expected, in hydrogen (not in carbon) as compared with acetylene.

As to the content of the new substance in copper, the analytical data are unfortunately ambiguous; for we note the weights found of copper oxide converted into percentages of copper without preliminary reduction. If the fault is typographical and in the analytical data, the calculated percentages of copper being correct, the average percentage of copper amounts to 15.43; if, on the other hand, the analytical data are right, the error being in their reduction, the percentage of copper amounts to 12.92. In the one case the summation of the analysis leaves a deficiency of about 1.5 per cent, and in the other of about 4 per cent, which in either case may really represent oxygen in the substance. This condition of matters leaves the "acetylen-kupfer" of Erdmann and Köthner in uncertain standing.

More than thirty years ago it was noticed by Berthelot (*Ann. d. Chim. et d. Phys.* [4], ix., 448) that acetylene is polymerised by heat or decomposed partially into carbon and hydrogen, and that such action takes place more readily and at lower temperatures in presence of metallic

iron with production of carbon, hydrogen, and compounds different from those formed by heat alone.

Moissan and Moureu (*Comptes Rendus*, cxxii., 1240) have observed the incandescence of acetylene passed over finely divided iron, cobalt, nickel, or platinum, at the ordinary temperature, with production of carbon, hydrogen, and pyrogenic compounds, and have found the occasion of such behaviour in the porosity of the metals employed.

It would seem natural, however, that the presence of oxygen, free or combined, may also play a considerable part in such phenomena, just as appears to be the case in the peculiar action recorded by Gruner (*Ann. d. Chim. et d. Phys.*, [4], xxvi., 5) of carbon monoxide upon iron reduced by hydrogen, which, as Moissan has shown (*Ann. d. Chim. et d. Phys.* [5], xxi., 199), is produced pure only with the greatest precaution, and generally carries a large proportion of ferrous oxide. The fact that the "acetylen-kupfer" of Erdmann and Köthner is produced more easily by the action of cuprous oxide upon acetylene than by the action of metallic copper upon acetylene, suggests that it may be the oxidising power of the cuprous oxide which gives to this reagent its peculiar activity. The question arises, therefore, as to whether the copper is in reality an essential constituent of the compound of Erdmann and Köthner.

In our experiments upon the action of acetylene upon the oxides of copper (and other elements) we have conducted the gas (made in the ordinary way by the action of water on calcium carbide, and kept over water) over the oxide contained in a porcelain boat placed within a glass tube, 2 c.m. in diameter and 50 c.m. long, which was heated over a small combustion furnace. The glass tube was fitted at each end with a rubber stopper, one carrying a smaller tube for the introduction of the acetylene and a high-temperature thermometer so held that its bulb rested horizontally immediately over the boat containing the oxide, while the other was fitted with a water-trap. In the preliminary experiments no attempt was made to purify the acetylene employed other than to keep it over water, or, since water is a product of its action upon oxides, to dry it: in later experiments, to secure products for careful analysis, it was dried and purified with care.

We found that 225° C. is the temperature most favourable for the formation of the voluminous product obtained by acting with acetylene upon cuprous oxide as described by Erdmann and Köthner. At this temperature the tube is choked rapidly with the fluffy product, and water forms, but, as Campbell found in his experiments upon palladinised copper oxide, no appreciable amount of carbon dioxide is produced. The content of the product in copper varies in the sample and in different experiments, our results lying between 1.54 per cent and 24.21 per cent of the substance taken for ignition.

It appeared, also, that the action of acetylene upon cupric oxide is precisely similar to that upon cuprous oxide excepting the evident reduction of the former oxide early in the action. The amount of copper in the product of such action varied in our experiments from 6.53 per cent to 21.30 per cent. In one case the experiment of re-submitting to the action of acetylene a product containing 9.34 per cent of copper was made with the result that a new growth of the substance formed which on analysis yielded 3.87 per cent of copper.

A roll of copper gauze carefully reduced in hydrogen and then oxidised at one end in the outer flame of a Bunsen burner, gave, when acted upon by acetylene at 225–250° C., the characteristic deposit upon the oxidised end only, the unoxidised end being merely discoloured.

These results go to show that, while metallic copper may at comparatively high temperatures induce the polymerisation of acetylene, it is an oxidising action which starts at moderately low temperatures the formation of the peculiar derivatives under consideration. Thus we find that ferric oxide heated in acetylene at

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, viii., Nov., 1899.

	Weight of substance taken. Grm.	Found.			Calculated.			
		CO ₂ .	H ₂ O.	CuO.	C.	H.	Cu.	O by difference.
		Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0.1170	0.3978	0.0673	0.0022	0.1085	0.0075	0.0018	-0.0008
2.	0.2247	0.7489	0.0979		0.2042	0.0109		
3.	0.1096	0.3678	0.0488	0.0045	0.1003	0.0054	0.0036	0.0003
4.	0.1360	0.4116	0.0579	0.0182	0.1123	0.0064	0.0146	0.0027
5.	0.1188	0.3 98	0.0461	0.0317	0.0845	0.0051	0.0253	0.0039
I.								
Per cent of carbon			92.74		90.88	91.51	82.57	71.13
„ hydrogen			6.41		4.85	4.93	4.71	4.29
„ copper			1.54			3.29	10.74	21.30
„ oxygen			—			0.27	1.98	3.28
				100.69			100.00	100.00
II.								
Per cent of carbon			94.93		93.54	94.93	94.60	94.31
Per cent of hydrogen			5.07		6.46	5.07	5.12	5.40
				100.00			100.00	100.00

temperatures varying from 150° to 360°, according to circumstances, darkens, glows, and gathers with evolution of heat a dark carbonaceous deposit. In the products of such action we have found the content of iron varying from 2.80 per cent to 5.86 per cent.

Silver oxide, too, acts upon acetylene: thus, in one experiment, action was evident at the ordinary atmospheric temperature, a violent explosion, which completely shattered the boat and scattered metallic silver upon the sides of the glass tube, following before the temperature reached 100°.

In the locally violent explosion of the last experiment we have evidence of the formation in the early stage of an acetylide which is decomposed later when the temperature of dissociation is reached. In the experiments with the oxides of copper and iron, the temperature at which the acetylene begins to act is evidently above the point at which sensitive acetylides would naturally dissociate, and we have in the observed phenomena no evidence of the formation of such compounds of copper and iron under the conditions of experimentation.

In experiments 1 to 3 of the accompanying table are given the results of the analysis of several products obtained by conducting acetylene (purified by passing through a solution of mercuric chloride in hydrochloric acid and dried over caustic potash) over pure cuprous oxide. The temperature was kept in these experiments at 225°, and in the course of a half hour the tube was choked completely by material compacted by the pressure to 1, a spongy mass of light brown colour on the exterior next the walls of the tube; 2, darker within; and 3, nearly black in the bottom of the boat, where the cuprous oxide lay originally.

In experiments 4 and 5 the substances analysed represent the products of the action of acetylene (not specially purified) on cupric oxide.

The oxygen present in these products is obviously proportional to the amount of copper, and is never more than enough to be completely accounted for upon the supposition that some of the original oxide taken still holds its oxygen. So far as the analyses show, the product of lightest colour, 1, contains little copper and no oxygen; the darkest product, 3, obtained from the cuprous oxide contains oxygen corresponding to a mixture of two parts of copper with three parts of cuprous oxide; the oxygen in the products of 4 and 5, obtained by acting upon cupric oxide, is approximately enough to correspond to a mixture of cuprous and cupric oxides in equal proportions. This fact, taken in connection with the great range of variation in proportion and the minimum to which the copper falls in the product, which would be least likely to include contaminating metal or oxide, suggests very strongly the probability that the oxygen present is in union with copper, and that the copper is held mechanically as metal or oxide, and is not the essential constituent of an organic compound. Leaving out of consideration, therefore, the copper and copper oxides, and calculating the compo-

sition of the products assumed to consist essentially of carbon and hydrogen, we derive the following statement:

Per cent of carbon	1. 93.54	2. 94.93	3. 94.88	4. 94.60	5. 94.31
Per cent of hydrogen	6.46	5.07	5.12	5.40	5.69
	100.00	100.00	100.00	100.00	100.00

These figures correspond to symbols varying from C₁₂H₁₀ to nearly C₁₆H₁₀, with an average approximating C₁₄H₁₀, the symbol of anthracene or paranthracene. The analytical data of Erdmann and Köthner point in the average to a product corresponding more nearly to the first of these symbols than to either of the others. The product is doubtless variable with the temperature and the activity of oxidation. Thus, in one experiment in which acetylene was passed over ferric oxide, the action began at 365° with incandescence, as described by Moissan and Moureu (*loc. cit.*), and the analysis of the product (carbon = 91.53, hydrogen = 1.36, Fe = 5.85, O = 1.26) indicates a proportion of carbon to hydrogen about four times as great as that of the average product of action at 225° on the oxides of copper.

Finally, we find no evidence that the product of the action of acetylene on the oxides of copper under the conditions of our experimentation is other than a mixture of a hydrocarbon or hydrocarbons with metallic copper or an oxide of copper, and, probably, in the darker preparations, some free carbon.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 21st, 1899.

Professor THORPE, F.R.S., President, in the Chair.

DR. KOHN was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Granville Reginald Gee, Falcon Villa, Howard Street, Gloucester; Alfred William Harvey, 13, Pendrell Road, St. Catherine's Park, Hatcham, S.E.; Thomas Ebenezer Mackenzie, 6, Cardonald Terrace, Cardonald, near Glasgow; William Mair, 388, Morningside Road, Edinburgh; John Livingston Rutgers Morgan, 47, Bayard Street, New Brunswick, U.S.A.; James Fraser Readman, 50, Jane Street, Glasgow; James McConnell Sanders, 37, Summerhill Road, Dartford; and of Sidney Calvert, Missouri State University, Columbia, Missouri, whose Certificate was approved by Council under Bye-law I. (3).

The SECRETARY read the following letter, written by the President at the request of the Council, to Professor Emil Fischer, a Foreign Member of the Society, con-

gratulating him on the completion of the twenty-fifth year of his Doctorate, together with a translation of Professor Fischer's reply.

16th November, 1899.

MY DEAR COLLEAGUE,—As President of the Chemical Society, I have the pleasure to offer you, by request of the Council, the warmest congratulations of the Fellows on the completion of the twenty-fifth year of your Doctorate.

It is not often that so short a span of intellectual activity in the life of any one individual comprehends such a brilliant series of scientific triumphs as those with which you have enriched chemistry.

That you may long be spared to cultivate the many fields of fruitful inquiry you have so assiduously opened up is the fervent wish of this Society, which recalls with pride that it numbers you amongst the most distinguished of its Foreign Members.—I have the honour to be, with great respect, my dear Colleague, your obedient humble Servant,

T. E. THORPE, President.

To Professor Dr. EMIL FISCHER, Berlin.

The following is the translation of Professor Fischer's reply:—

10, Dorotheenstrasse, Berlin,
29th November, 1899.

HIGHLY ESTEEMED PRESIDENT,—I have been most agreeably surprised by the honour as well as the heartiness of the congratulations which you have conveyed to me in the name of the Chemical Society, on the occasion of the celebration of the 25th year of my Doctorate. Your Society and other learned bodies in England have indeed done me so much honour that I am obliged to ask myself, with diffidence, whether it bears any relation to my achievements.

The time when the fundamental principles of our Science were laid down, and when it was possible for the individual investigator to stamp the impress of his own mind upon it, is long since past, and, in the gigantic structure which it now represents, each fellow worker can only finish some small fragment, or it may be, if he is fortunate, a pretty balcony or a striking turret. The progress of the whole is, however, most readily accomplished by the combined efforts of numerous gifted and skilled observers. This co-operation, so characteristic of the scientific work of the present day, is exhibited in its highest form by the great Chemical Societies, of which yours is the oldest and has served as a model for the others.

I am proud, therefore, to be allowed to belong to it as a Foreign Member, and I beg, esteemed President, that you will be so good as to convey to your Council my heartfelt thanks for their kind congratulations.—With the highest esteem, yours obediently,

EMIL FISCHER.

Prof. Dr. THORPE,
President of the Chemical Society, London.

Of the following papers, those marked * were read:—

*163. "On the Refractive and Magnetic Rotatory Powers of some Aromatic Hydrocarbons, and on the Refractive Powers of Mixtures." By W. H. PERKIN, LL.D., F.R.S.

The first part of the paper deals with a comparison of the magnetic rotatory and refractive powers of aromatic hydrocarbons undertaken to see if these properties were analogous in character. Most of the hydrocarbons employed were of exceptional purity, many being prepared from the pure salts of their sulphonic acids. An account is given of the preparation and properties of *isobutylbenzene*, prepared by this method for the first time.

With regard to the refractive powers of these substances, the results obtained show that the replacement by methyl of a hydrogen atom in the nucleus gives a value considerably larger than when the replacement takes place outside, and this is so certainly up to four such re-

placements, and therefore probably for the six. The replacement of hydrogen outside the nucleus by methyl (as in the conversion of toluene into ethylbenzene) also gives results somewhat higher than those calculated, but these values tend to coincide more nearly as the distance from the nucleus increases.

With the magnetic rotations the reverse was found to hold, as a considerably smaller increase in the rotation is produced by a change in composition of CH_2 in the nucleus, than when it occurs outside. This holds for four replacements, and therefore probably for all.

These results are remarkable when the general correspondence between the magnetic rotatory and refractive powers of compounds is considered.

The second part refers to the refractive powers of mixtures. It has been shown that in the case of the magnetic rotations of mixtures these are usually less than those calculated from the molecular rotations of the constituents when their specific rotations are widely apart; hence it was of interest to determine whether a similar difference existed in the case of the refractive powers of mixtures. It was found that when the two constituents had very widely differing indices of refraction, the specific or molecular refraction was considerably lower than that calculated, but that when indices were nearly the same the calculated and observed values agreed very well. That this latter statement holds was shown by means of a mixture (a) of fatty compounds, (b) of aromatic compounds. These differences were most marked in mixtures of two fatty compounds having indices widely apart; in mixtures of a fatty with an aromatic compound they were less pronounced.

Many of Zecchini's experiments with mixtures give results of a similar character to those described above, but exceptions occur which seem to indicate that although the differences between the refractive powers of the substances employed appear to be the chief cause of these peculiar results, other causes must also be at work. A new and improved arrangement for reading the scale and vernier of the spectrometer was described and shown.

DISCUSSION.

The PRESIDENT, after recalling the fact that differences similar to those observed by the author had been also observed with regard to the viscosity of pure compounds and mixtures of them, inquired why mixtures in equal volumes rather than in molecular proportions had been employed in this investigation.

Dr. GLADSTONE remarked that the results of the author to a certain extent explained some of the difficulties met with by early workers in the field of molecular refraction, and that many of them had observed similar small differences which were yet quite beyond the limit of experimental error. There was no doubt that researches such as those of Dr. Perkin must tend to throw more and more light on the causes of these small divergences in the optical properties and hence to reveal more fully the structure of the molecule.

Dr. PERKIN, in reply, said that the use of mixtures of equal volumes of the constituents had originated in his work on magnetic rotation, as such mixtures allowed of more ready comparison of the indices of refraction, densities, &c., of the mixtures and their components,

164.* "Formation of α - and β -Acrose from Glycollic Aldehyde." By HENRY JACKSON, B.A.

When a dilute (3 per cent) aqueous solution of glycollic aldehyde is allowed to stand with a 1 per cent solution of soda for fifteen hours at 0° , it is still able to reduce Fehling's solution in the cold (though not so strongly as a solution of glycollic aldehyde), and to restore the colour to an alcoholic solution of magenta which has been decolourised by sulphurous acid. If the condensation product be neutralised with acetic acid, then heated on the water-bath with phenylhydrazine acetate, an osazone is obtained which, on purification and fractional treatment with various solvents, can be shown to contain tetrosazone

[obtained previously by Fischer and Landsteiner (*Ber.*, 1892, xxv., 2549), by condensing glycollic aldehyde with soda at 0°, and two hexosazones, α -acrosazone m. p. 217°, and β -acrosazone, m. p., 158°.

If the condensation be allowed to proceed for a longer time at 0°, it is found that the power of reducing Fehling's solution in the cold gradually diminishes until, after standing six days, it no longer reduces in the cold, but quickly on warming. The osazone obtained consists almost entirely of a mixture of the two hexosazones (α and β -acrosazone), only a trace of tetrosazone being found.

DISCUSSION.

Mr. FENTON said that it was evident, both from these and from previous observations, that the condensation products of glycollic aldehyde and of formaldehyde were identical. It was probable that glycollic aldehyde was an intermediate stage in the condensation of formaldehyde, especially as Pechmann (*Ber.*, 1897, xxx., 2459) had shown that the osazone of glycollic aldehyde could be obtained directly from formaldehyde and phenylhydrazine in acetaldehyde solution.

165. "The Interaction of Mercurous Nitrite and Ethyl Iodide." By P. C. RAY, D.Sc.

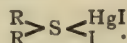
When mercurous nitrite acts upon ethyl iodide, about equal quantities of nitroethane and its isomeride, ethyl nitrite, are formed. The yield is, however, somewhat poorer than when silver nitrite is used, owing to the formation of very compact lumps of mercurous iodide, which prevents the reaction from becoming complete.

166. "On Mercurous Iodide." By P. C. RAY, D.Sc.

When the residue in the flask after the interaction of mercurous nitrite and ethyl iodide is heated in a tube, mercurous iodide sublimes off between 190° and 210°. The compact mass of crystalline tablets thus obtained shows all gradations of tint from lemon- and orange-yellow to dark brown.

167. "The Action of Alkyl Iodides on the Mercuric Iodide Sulphides of the Fatty Series." By SAMUEL SMILES, B.Sc.

The alkyl sulphides unite with mercuric iodide to form compounds of the general formula R_2SHgI_2 . Like other addition products of the sulphides, their constitution should be represented as—



The following members of the series were examined:—

Me_2SHgI_2 , long, yellow needles from acetone, m. p. 75°.

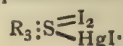
$MeEtSHgI_2$, short prisms from acetone, m. p. 59°.

Et_2SHgI_2 , yellow prisms from acetone, m. p., 52°.

$(C_5H_{11})_2SHgI_2$ (isoamyl), yellow oil.

$(C_7H_7)_2SHgI_2$, pale yellow plates from acetone, m. p. 37—38°.

These substances are unstable, readily splitting off mercuric iodide when exposed for any length of time to the air, or when boiled with water. Dimethylsulphide mercuric iodide, when treated with methyl iodide, yields the same product as that obtained from trimethylsulphine iodide and mercuric iodide, namely Me_3SIHgI_2 . The same holds good for the triethyl derivative. Hence the double salts formed from mercuric iodide and sulphine iodide appear to contain hexavalent sulphur, as their constitution may be represented as—



Therefore, it was hoped that an investigation of the derivatives containing different alkyl groups would yield evidence as to the stereo-chemical nature of hexavalent sulphur. So far, however, only negative results have been obtained.

The following substances were prepared and examined:

Me_3SI_2HgI , large, yellow prisms from acetone, m. p. 165°.

From—(1) Me_3SI and HgI_2 ; (2) Me_2SHgI_2 and MeI . Me_2EtSI_2HgI , long, yellow prisms from acetone, m. p. 87°.

From—(1) Me_2EtSI and HgI_2 ; (2) Me_2SHgI_2 and EtI ; (3) $MeEtSHgI_2$ and MeI .

$MeEt_2SI_2HgI$, bright yellow prisms from acetone, m. p. 67°.

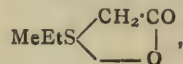
From—(1) Et_2MeSI and HgI_2 ; (2) Et_2SHgI_2 and MeI ; (3) $MeEtSHgI_2$ and EtI .

Et_3SIHgI_2 , bright yellow leaflets from acetone, m. p. 112°.

From—(1) Et_3SI and HgI_2 ; (2) Et_2SHgI_2 and EtI .

Just as in the case of the nitrogen compounds such isomerism as might be expected here may be prevented by the presence of methyl or ethyl groups, it will therefore be necessary to repeat this with derivatives containing more complex radicles.

Attempts were also made to resolve methyl ethyl thetine,—



into optically active components, but without success.

168. "On Brasilin and Hæmatoxylin. Part III." By A. W. GILBODY and W. H. PERKIN, jun.

In a previous communication (*Proc.*, 1899, xv., 27), an acid obtained from brasilin was described which melted at 155° and gave, on analysis, numbers agreeing with the formula $C_{15}H_{16}O_6$. This acid, on oxidation with potassium permanganate, yielded a dibasic acid melting at 200—203°, which, when heated with hydrochloric acid at 160°, was decomposed with formation of catechol. Further investigation has shown that this acid, which at first was thought to have the formula $C_{10}H_{10}O_3(CO_2H)_2$, is in reality *metahemipinic acid*,



This has been conclusively proved by converting the acid into its anhydride and characteristic ethylimide (m. p., 230°). *Tetramethylhæmatoxylin*, when oxidised with chromic acid, also yields considerable quantities of *metahemipinic acid*, a proof that hæmatoxylin, like brasilin, is a derivative of catechol. As this result does not agree with the statement of R. Meyer (*Ber.*, 1879, xii., 1393) that hæmatoxylin, on distillation, yields pyrogallol and resorcinol, we have repeated this work, and find that the products of the destructive distillation of hæmatoxylin contain considerable quantities of pyrogallol, but, as far as we could determine, no trace of resorcinol.

It follows, therefore, from these experiments, that whereas brasilin is a derivative of resorcinol and catechol, hæmatoxylin is a derivative of pyrogallol and catechol.

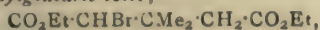
The formation of metahemipinic acid from both brasilin and hæmatoxylin shows that the formulæ which we suggested for these substances require some modification. It would be easy to construct formulæ which would take these new facts into account, but we prefer to wait until further experimental evidence is forthcoming before doing so. We hope, therefore, that others working in this field will allow us to reserve for a short time the deduction of any formulæ for brasilin and hæmatoxylin which are based on the new results described in this and the two preceding preliminary communications.

It should be noticed that the melting-point of tetramethylhæmatoxyline is incorrectly given as 170° in the previous communication, it should be 183—186° with vigorous decomposition.

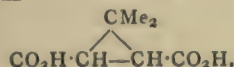
169. "The Action of Alcoholic Potash on Monobromoglutaric Ester." By N. E. BOWTELL and W. H. PERKIN, jun.

A short time since (*Trans.*, 1899, lxxv., 50) it was

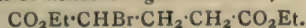
shown by J. F. Thorpe and one of us that when *mono-bromodimethylglutaric ester*,—



is digested with alcoholic potash, it yields a mixture of *cis*- and *trans*-dimethyltrimethylenedicarboxylic acids (caronic acids),—



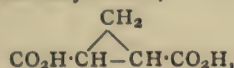
It occurred to us that it would be interesting to investigate the behaviour of *monobromoglutaric ester*,—



under similar conditions, as in this case there are two possibilities, namely, either glutaric acid,—



or trimethylenedicarboxylic acid,—



could be formed.

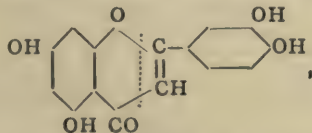
Monobromoglutaric ester was obtained as a colourless oil boiling at 165—170° (35 m.m.) by brominating glutaric anhydride and pouring the product into alcohol. When this ester is decomposed by alcoholic potash, an acid is obtained melting at 175°, which on examination was found to consist of *trans*-trimethylenedicarboxylic acid, and we were unable to isolate even traces of glutaric acid.

This remarkable result points to the possibility that many substances produced by similar reactions and described as unsaturated may in reality be derivatives of trimethylene, tetramethylene, &c.

We are engaged in investigating the action of alcoholic potash on the esters of bromine substitution products of adipic, pimelic, and allied acids.

170. "Luteolin. III." By A. G. PERKIN.

Previous investigations (*Trans.*, 1896, lxi., 206, 799) indicated that luteolin, $\text{C}_{15}\text{H}_{10}\text{O}_6$, is a tetrahydroxyflavone. The energetic action of alkali yielded phloroglucinol and protocathechuic acid, confirming Rochleder's results (*Zeit. für Chem.*, 1866, ii., 602), and it is now found that, by gentler treatment, phloroglucinol and a substance having the composition $\text{C}_8\text{H}_8\text{O}_3$ are formed. ($\text{C} = 63.16$; $\text{H} = 5.26$. Found $\text{C} = 63.47$; $\text{H} = 5.61$). The substance (colourless needles, melting-point 115—116°) gives, with fused alkali, protocathechuic acid, and its properties are identical with those of *acetylcathecol*, $\text{CH}_3\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ (Dzergowski, *Journ. Russ. Chem. Soc.*, 1893, xxv., 157). This confirms the constitution assigned by the author to luteolin,—



and is identical in its nature with the decompositions of chrysin, $\text{C}_{15}\text{H}_{10}\text{O}_4$ (Kostanecki, *Ber.*, 1893, xxvi., 2901), and apigenin (*Trans.*, 1897, lxxi., 805), which respectively yield phloroglucinol and acetophenone, and phloroglucinol and *p*-hydroxyacetophenone.

In conjunction with Mr. L. H. Horsfall, an investigation is in progress upon certain ethers of luteolin. By partial methylation, a *dimethyl ether* (found $\text{C} = 65.06$; $\text{H} = 4.55$; $\text{CH}_3 = 9.92$), colourless needles, m. p. 227—229° is formed in small quantity; this is almost devoid of dyeing property, and by means of alkali gives *isovanillic acid*. There is evidence that, in addition to luteolin, weld contains a trace of a second colouring matter.

171. "The Action of Chloroform and Potassium Hydroxide on Orthoamidobenzoic Acid." By WALTER J. ELLIOTT, M.A.

By acting on orthoamidobenzoic acid with chloroform and potassium hydroxide, acidifying the product with acetic acid, and treatment with phenylhydrazine and semicarbazide respectively, the author has obtained the phenylhydrazone and semicarbazone of an aldehydo-orthoamidobenzoic acid. Owing to its great solubility in water, he has failed to obtain the free aldehydo-acid in a state of purity. The barium and silver salts of the phenylhydrazone have been prepared and analysed. The hydrazone and semicarbazone are both very stable.

172. "Azo- and Hydrazone Compounds Differentiated by Bromine." By H. E. ARMSTRONG.

Although the constitution of the "oxyazo" compounds has been the subject of numerous investigations, apparently chemists are not yet in agreement as to their formulæ; indeed, only recently, Hantzsch in Germany, and MacPherson in America, have arrived at diametrically opposite conclusions. The difficulty arises from the fact that parahydroxyazobenzene—the parent of all "oxyazo" compounds—and quinonephenylhydrazone are unquestionably isodynamic. Methods such as Hantzsch and Farmer have adopted must, therefore, be regarded as in principle the only suitable ones for the determination of structure in such cases, and extreme care must be taken in interpreting interrelations.

A number of observations made in the author's laboratory by Messrs Panisset, Seligmann, and Isherwood are of interest as bearing on the problem.

The stability of diazobenzene in presence of bromine was established by Griess in his earliest investigation. Diazobenzeneparasulphonate is also untouched by bromine, and action only takes place gradually as it becomes hydrolysed. Azobenzene is only very slowly and imperfectly acted on by bromine. Nitrogen, in fact, by no means tends to promote substitution, unless associated with hydrogen.

If oxyazobenzene were parahydroxyazobenzene, one would expect it to be readily brominated in the ortho-position relatively to the hydroxyl; but, as a matter of fact, it yields a product convertible into parabromaniline and phenol on reduction, and which is easily prepared from these, a result only compatible with the view that towards bromine it behaves as a hydrazone.

This view is confirmed by the fact that when the ethylated compound is brominated, a substance is formed which Mr. Isherwood finds to be identical with that produced on coupling orthobromophenol with diazobenzene and then ethylating. It is noteworthy that the bromine is removed from this compound with exceptional facility, both when dissolved in acetone and when left in contact with sulphurous acid.

The behaviour of bromine in excess towards the quinhydrazones is characteristic. Quinonebromophenylhydrazone is resolved by it into bromodiazobenzene and tribromophenol, and ordinary tropæolin into diazobenzenesulphonate and tribromophenol. So complete is the change in this latter case, that if, after the tribromophenol has been filtered off, phenol be added to the solution, and then alkali, an amount of tropæolin can be recovered almost equal to that originally taken.

Victor Meyer Memorial Lectures.

The Victor Meyer Memorial Lecture will be delivered by Professor T. E. Thorpe, President of the Society, on the evening of Thursday, February 8, 1900, at 8.30.

The Decomposition of Alkaline Hypochlorites.—J. Thomsen.—The author shows that some of the results recently obtained by Foerster and Jorø agree with those already obtained by him (*Thermochem. Untersuch.*, ii., 123). The aqueous solutions of hypochlorous acid, as well as solutions of hypochlorite of soda containing an excess of acid are rapidly decomposed.—*Journ. für Prakt. Chem.*, 1899, lix., p. 244.

CORRESPONDENCE.

RELATIONS BETWEEN THE
ATOMIC WEIGHTS AND PHYSICAL PROPERTIES
OF ELEMENTS.*To the Editor of the Chemical News.*

SIR,—In my note (CHEM. NEWS, lxxx, p. 314) I pointed out that the product of melting-point (absolute) $\times$ coefficient of linear expansion for 1°C. is a constant for a number of elements, and that this product has higher and varying values for several other elements. The coefficients were (as I indicated) determined by various observers and at various (disproportionate) temperatures, but they were the best available. I did not attempt to explain the different values of the product.

The idea of absolute zero and the absolute scale of temperature arose from the study of the properties of the permanent gases (as they were then considered) at an early period in the history of modern science. But, as long ago as 1848, Wm. Thompson (now Lord Kelvin) based a scale of absolute temperature upon the fundamental principles of thermodynamics, and showed that the zero of this scale is really absolute,—that is, if it is zero for one substance it is zero for every other. Lord Kelvin and Joule have since determined experimentally, by means of the cooling effect produced in a fluid when forced through a small orifice or porous plug, that zero on this scale coincides with that originally deduced from the thermal expansion of gases. The results of their experiments on hydrogen, air, and CO_2 , gave the absolute temperatures of melting ice as 273° , 273.14° , and 273.9° respectively.

This refers the expansion of gaseous bodies to absolute zero as deduced on independent mathematical grounds: and as showing that a physical property of solids is referable to the same starting-point, the experiments of Dewar and Fleming may be mentioned. These investigators found that the electrical resistance of certain pure metals, of which platinum is one, diminishes at low temperatures in such a way as to show that it tends to vanish at -273°C. At this temperature all heat has disappeared, and consequently the resistance caused by it.

It therefore appears as if the title which Mr. Wertheimer writes of as "only a survival from the infancy of modern chemistry" is likely to survive well into the twentieth century, whether this begins in 1900 or 1901. In asserting a different value to the absolute zero for zinc and cadmium he seems necessarily to be assigning a positive value to zero in one instance or the other.

The germ of a valuable idea is contained in Mr. Wertheimer's references to the coefficient of expansion taken at "similar" and "similarly located" temperatures. For just as it is necessary to measure the coefficient of a gas at a sufficient distance above its condensing point, so it is necessary to determine the coefficient of a solid at a point removed, and probably proportionately removed, from the melting-point.

As regards Mr. Wertheimer's suggestion that the coefficient of expansion $\times$ B.P. — M.P. might give universal constants, it must not be overlooked that boiling-points, unless taken in an absolute vacuum, must be arbitrary. Ordinarily they are given for the atmospheric pressure that happens to prevail on this planet. If interesting results should be found by this means, it is probable they would be due to the nature of c , where B.P. *in vacuo* $\times c = \text{B.P. at } 760 \text{ m.m.}$

The study of melting-points, boiling-points, and atomic volumes, by the graphical method, shows an interrelation to exist between these properties of the elements, —e.g., B.P./M.P. Zn = B.P./M.P. Cd.—I am, &c.,

THOMAS BAYLEY.

January 1, 1900.

NOTICES OF BOOKS.

Industrial Electricity. Translated and Adapted from the French of HENRY DE GRAFFIGNY, and Edited by A. G. ELLIOTT, B.Sc. London: Whittaker and Co. Pp. 152. With 65 Illustrations.

THE volume now before us is the first of a Series which it is proposed to issue on the subject of Electro-mechanics. This series is likely to be popular, inasmuch as the explanations are in clear and non-mathematical language. The present volume may be considered as introductory to the series, each chapter—of which there are XII,—dealing shortly with a separate branch of practical electricity.

The other volumes of the series will treat the more important branches of the subject separately and in detail.

A Synopsis of the British Pharmacopœia, 1898. Compiled by H. WIPPELL GADD, with Analytical Notes and Suggested Standards by C. G. MOOR, M.A., F.I.C. Fourth Edition. London: Baillière, Tindall, and Cox. 1899. 223 pp.

Now that the Pharmacopœia has been in use for over twelve months it has been thought desirable to omit the tables of alterations, additions, and omissions in this the fourth edition of the "Synopsis." The changes will be still found mentioned, however, in the general table, to which also specific gravities, alcoholic strengths, and percentage of solid residues have been added in many cases.

Appendices have also been added, giving particulars of test solutions, analytical methods, &c., the whole forming a very handy and compact pocket book.

WHO BUYS GAS PURIFYING MATERIAL
(Spent) for its contents of BLUE?

Gentleman, in constant touch with all the Gas Works of the United Kingdom, wishes to enter into a standing arrangement with Chemical Works to buy above material for their order.—Address, "Purifier," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

TO BUYERS OF SPENT GAS PURIFYING
MATERIAL.

Required, a Commission from SULPHUR WORKS to buy the above from all Gas Works in the United Kingdom. Advertiser is in a position continually to offer large quantities.—Address, "Sulphur," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

PATENTS, DESIGNS, AND TRADE MARKS ACTS
1883 TO 1888.

NOTICE IS HEREBY GIVEN, that OLIVER

IMRAY, of Birkbeck Bank Chambers, Southampton Buildings, Chancery Lane, in the County of London, has applied for leave to amend the Specification of Letters Patent No. 21839 of 1893, for the "MANUFACTURE OF DYESTUFFS OF THE DIPHENYLNAPHTHYLMETHANE SERIES."

Particulars of the proposed Amendment were set forth in the "Illustrated Official Journal" (Patents) issued on the 30th December 1899.

Any person, or persons, may give notice of opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

(Signed),

G. H. DALTON,
Comptroller-General.

ABEL & IMRAY,
Agents for the Applicant,
Consulting Engineers and Chartered Patent Agents.
Birkbeck Bank Chambers,
Southampton Buildings, London, W.C.

OXALIC ACID.

A French Manufacturer wishes to establish a Factory for making Oxalic Acid. He requires a Chemist or a Foreman who has already had the management of a Factory for Oxalic Acid. Good references required.

Address reply to—
Monsieur JOSEPH RUET, 7, Rue Saint Claud, Paris.

THE CHEMICAL NEWS.

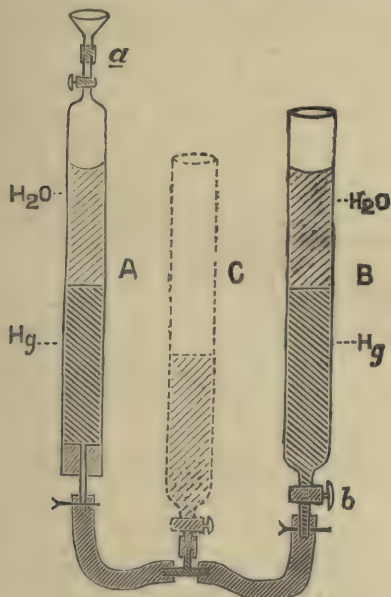
VOL. LXXXI., No. 2094.

LABORATORY NOTES.

ON THE SOLUBILITY OF SOME GASES IN WATER.

By WILLIAM FRENCH, M.A., and F. ASHWORTH, B.A.

THE apparatus in use for the determination of the solubility of the more sparingly soluble gases, oxygen, nitrogen, &c., viz., that of Bunsen, and Heidenhain and Meyer, whilst admirably adapted for working where great accuracy is required, seemed to one of us to be quite unnecessary for ordinary class work, or, when it is required to demonstrate (1) that these gases are appreciably soluble in water, (2) that oxygen is more soluble than nitrogen. The object of these experiments were taken, therefore, not with a view of confirming the results obtained by previous workers, but rather to see how far ordinary apparatus, such as will be found in any well-equipped laboratory, could be adopted for the purpose.



Our first experiments were carried out with a Lunge's nitrometer, and the numbers (representing solubilities) obtained approximated so near published numbers, that we were induced to repeat them with a piece of apparatus constructed from two (or three) burettes. The method of working was essentially the same whichever apparatus was used, with the exception that no funnel was required with a nitrometer.

A is an inverted stoppered burette, fitted with an india-rubber stopper, and connected by pressure tubing to another burette, B. A small funnel is fitted at A with rubber, and mercury is placed in B, which is raised until the metal begins to pass into the funnel; cold, well-boiled distilled water is added to the funnel, and B quickly lowered, so that about 30 c.c. of water pass into A; the funnel is removed, and the gas supply attached to A, and about 5 c.c. of the gas drawn in. Water is now added to B, so that the heights of the water in each side is the same when the mercury levels are the same (the reason of this is obvious), and the volume of water and gas

taken quickly read off. The stopcock B is now closed (or the tubing is pinched) and the burette A is well shaken; B is then opened, the levels equalised, and the diminution of gas noted; this is repeated until the diminution is constant. The volume of gas dissolved is reduced for temperature and pressure, and the solubility obtained in the usual way. A burette C (in dotted lines), fitted with a T-piece into the pressure tube, greatly facilitates quick working, it forming a reservoir for the mercury, but it is not essential. Using this apparatus for class work, students working in pairs may quite readily prove the statement so often made in text-books that oxygen is more soluble in water than nitrogen, and using great care very fair results may be obtained. The following numbers were obtained by Messrs. Howlett, Evans, Macfarlane, and Garnett; beneath these are numbers taken from "Bayley's Chemist's Pocket Book" for the same temperatures for comparison:—

Oxygen.	Nitrogen.	Air.	CO ₂ found.
0.02879 15°C.	0.0151 15°C.	0.01729 19°C.	0.952 15°C.
0.02989 "	0.01478 "	0.01719 "	1.002 "

Grammar School, Bury.

THE SEPARATION OF TUNGSTEN AND MOLYBDENUM.

By FRED IBBOTSON and HARRY BREARLEY.

OF the few methods one can find for effecting this separation, volatilisation of the molybdenum in a stream of hydrochloric acid gas is best known, and appears to be most commonly used. As a rule, tube volatilisations are made use of in metallurgical laboratories only as a last resource or for research purposes. On this account a separation which can be made in every-day apparatus and with common reagents was desirable.

Quite a number of circumstances can be arranged under which molybdenum and tungsten behave in diverse ways, but very few in which the behaviour, when the two elements are together, of the one is so sharply different from that of the other as to provide an accurate means of separating them. These methods chiefly depend on the solubility of the one and the insolubility of the other metal compounds (generally oxides) in certain acids, and they are deficient because the WO₃ is never perfectly insoluble, nor the MoO₃ perfectly soluble, except when alone.

The following experiments were made with the object of determining with what degree of accuracy one or two theoretically sound principles could be applied.

I. Volatilisation of Molybdic Oxide in the Muffle.

MoO₃ can be completely volatilised in an ordinary gas muffle if alone, and very approximately, though with difficulty, when precipitated along with WO₃.

Sodium tungstate, equivalent to 0.1340 grm. WO₃, and sodium molybdate, equivalent to 0.1500 grm. MoO₃, were precipitated with mercurous nitrate and mercuric oxide and ignited in the muffle. Long after the mercury had been vapourised white fumes of MoO₃ came from the crucible, but ceased to be visible some time before nearly all the molybdenum was got rid of. Ninety per cent of the Mo can be easily volatilised; the remaining 10 per cent needed several hours at a full red heat to drive it off. After reaching constant weight 0.1360 grm. WO₃ remained. According to Read (*Journ. Chem. Soc.*, lxxv, 313), WO₃ is stable at 1750°C. It might be easy if such temperatures were available to expel the MoO₃, but even then it would be troublesome to adapt the process so as to estimate the molybdenum directly.

II. Separation with Hydrochloric Acid Solution.

Precipitated amorphous MoO₃ is easily soluble in warm hydrochloric acid, but the variety, glistening and wool-

like, obtained by sublimation is not soluble in hydrochloric acid nor in *aqua regia*. This may account for the failure of attempts to separate ignited WO_3 and MoO_3 by treatment with HCl.

The solution of an alkaline molybdate, unless very strong, is not precipitated by adding hydrochloric acid; an emulsion of lead molybdate in water is completely dissolved by nitric acid; ignited lead molybdate is dissolved by hydrochloric acid, and not precipitated at all on diluting. On the other hand, WO_3 , after baking or igniting, is insoluble in HCl; the solution of an alkaline tungstate, if not too dilute, is precipitated by HCl; an emulsion of lead tungstate is decomposed by nitric acid with precipitation of WO_3 ; ignited lead tungstate is completely precipitated as WO_3 by diluting its solution in strong HCl, with two or three volumes of hot water.

Some of the above statements respecting tungsten are not absolutely true; they are so far from being true in fact, that in delicate analytical operations account must be taken of the errors which would creep in were they taken to be so. For instance, WO_3 is never absolutely insoluble in HCl. Prepared by decomposing an alkaline tungstate, or by diluting a hydrochloric acid solution of lead tungstate with water, WO_3 may be re-dissolved to a clear solution by concentrated HCl. After evaporation to dryness and baking, the solubility is less marked but still very appreciable. These facts are less obvious to casual observation, because nearly all the WO_3 is precipitated again on dilution. Even ignited WO_3 is not quite insoluble. By treating 0.4980 grm. ignited WO_3 with 60 c.c. strong HCl three times successively there were found:—

In Residue.	In Filtrate.
0.4945	0.0030
0.4910	0.0027
0.4876	0.0030
Lost from Residue.	Found in Filtrate.
0.0104	0.0087

From mixtures of one or two decigrams. of molybdenum and tungsten in the form of alkaline salts, the WO_3 precipitated by an acid is usually from 5 to 10 per cent too high, a result due, of course, to contamination with MoO_3 . The error is about the same if the moist PbWO_4 and PbMoO_4 are dissolved in HCl, and the WO_3 precipitated by diluting.

By re-dissolving the WO_3 in HCl and re-precipitating, the WO_3 generally weighs two or three m.grms. too little, due to the fact that at each precipitation a little WO_3 remains in solution, and that after the second precipitation less MoO_3 accompanies it than compensates for such loss. These small errors can never be entirely eliminated in any separation in HCl solution, but they may be minimised in either of the following ways:—

(A). Precipitate the Mo and W together by means of lead acetate, wash slightly with hot very dilute acetic acid, and ignite. Transfer to a beaker and dissolve in concentrated HCl, using about as many c.c. of acid as centigrams. of the lead salts.

The precipitates are most conveniently dissolved by heating just short of the boiling-point of the acid; in this way very few irritating fumes are evolved, and the acid is not weakened to any considerable extent before complete solution has been effected. To the clear or possibly faintly opalescent solution, add two or three times its bulk of boiling water, boil, allow to settle, decant clear liquid through a small pulp filter, re-dissolve in about half the quantity of acid previously used, re-precipitate with water, and filter through the same pulp. The Mo is determined in the filtrate, either with or without removing the HCl, by precipitation as PbMoO_4 (CHEM. NEWS, lxxviii., 203).

A number of experiments, which need not be quoted, show that the complete decomposition of PbWO_4 can be relied on only by dissolving in strong HCl and precipitating by dilution; diluted HCl does not completely decompose PbWO_4 after ignition.

If twice as many c.c. of acid are used as there are centigrams. of the lead salts, the tungsten is completely precipitated by diluting to three times the volume of the solution. Generally, larger amounts of acid used to dissolve the ignited precipitates require proportionally larger amounts of water for complete precipitation of the WO_3 . The estimation is not then so satisfactory, as the greater the dilution the greater the liability to contamination with MoO_3 .

The process just described gave the following results:—

	Added.	Found.	Error.
Mo	0.0918	0.0908	-0.0010
W	0.1031	0.1037	+0.0006
Mo	0.0551	0.0549	-0.0002
W	0.1031	0.1028	-0.0003
Mo	0.0367	0.0374	+0.0007
W	0.1031	0.1023	-0.0008
Mo	0.0184	0.0193	+0.0009
W	0.1031	0.1017	-0.0014
Mo	0.0092	0.0092	0.0000
W	0.1031	0.1023	-0.0008

Where the amount of Mo is very small, as in the last sample, it is not necessary to precipitate the WO_3 twice.

(B). If the amount of W is small compared with the Mo, it is not by any means totally precipitated on diluting to the usual volume. The following method, which gives as good results under any circumstances as the preceding, should then be adopted:—

The HCl solution of the ignited lead salts, to which a few drops of HNO_3 have been added, is evaporated, preferably over the water-bath, until nearly pasty, when the WO_3 will have almost entirely separated. The mass is then diluted with 100 to 200 c.c. dilute HCl (3 water to 1 acid), the solution boiled, and the WO_3 filtered off. The weak acid precipitates any WO_3 still unseparated by the evaporation, and is yet strong enough to hold the molybdenum in solution.

Whether the evaporation be performed slowly over the water-bath, or more rapidly, some of the WO_3 always adheres to the vessel and cannot be cleared off. A good plan for estimating this consists in dissolving it in 2 or 3 drops of dilute ammonia. The solution is then absorbed by a piece of ashless paper which is ignited along with the main portion of the precipitate. Appended are some test analyses:—

Added.	Found.	
0.1310	0.1290	WO_3
0.3510	0.3500	PbMoO_4
0.0780	0.0760	WO_3
0.3510	0.3510	PbMoO_4
0.0520	0.0510	WO_3
0.3510	0.3515	PbMoO_4
0.0131	0.0120	WO_3
0.3510	0.3495	PbMoO_4
0.0050	0.0040	WO_3
0.3510	0.3500	PbMoO_4

In some notes on the estimation of tungsten by one of us (CHEM. NEWS, lxxix., p. 64), it is shown that a precipitate corresponding exactly to the formula PbWO_4 is not obtainable by adding lead acetate to a soluble tungstate when there is any excess of acetic acid present, but is invariably acid in character, nor is tungsten completely precipitated in the presence of excesses of acetates and chlorides. As these very conditions of precipitation are favourable to the complete precipitation of molybdenum as PbMoO_4 , it was thought advisable, as a fitting conclusion to this paper, to see whether the precipitation of the two metals together under these circumstances would yield a mixture of true lead salts or not.

The following is a typical result:—

With an excess of 10 c.c. acetic acid, the weight of mixed lead salts was 0.5030, containing on analysis 0.0800 WO_3 instead of 0.0786, and 0.3500 PbMoO_4 .

instead of 0.3510 added. 0.0786 WO_3 represents 0.1541 PbWO_4 , which, added to 0.3510 PbMoO_4 , gives 0.5051 as the weight of mixed salts instead of 0.5030 actually got.

In the following analyses an amount of W corresponding to 0.1256 WO_3 , and of Mo corresponding to 0.4256 PbMoO_4 , were present in each case, so that, on the supposition of their being true lead salts, the weight of the mixed precipitates should be 0.6719 gm. For 0.1256 WO_3 represents 0.2463 PbWO_4 , and 0.2463 + 0.4256 = 0.6719.

	Wt. mixed lead salts.	WO_3 .	PbMoO_4 .
15 c.c. acetic acid	0.6771	0.1248	0.4247
Sodium acetate correspond- ing to 10 c.c. acetic acid.	0.6690	0.1232	0.4232
Ammonium acetate corre- sponding to ditto	0.6760	0.1241	0.4221
Ammonium chloride corre- sponding to 10 c.c. strong HCl	0.6792	0.1278*	0.4252

NOTE.—The noteworthy feature of these results is the indication that in the presence of not less than an equal amount of MO_3 , the W is not precipitated as an acid salt even when the solution contains considerable amounts of free acetic acid; and that the alkaline acetates and chlorides exert a comparatively insignificant solvent action under the same conditions. The feasibility of directly determining only one acid and calculating the other from the combined weight— $\text{PbWO}_4 + \text{PbMoO}_4$ —has been questioned, but our results now show that the plan merits greater reliance than could be claimed for it in view of the difficulty of obtaining pure PbWO_4 when W is precipitated separately. They show, in fact, that the combined lead salts are actually somewhat basic and not acid.

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THE

ELECTROLYTIC ESTIMATION OF MANGANESE IN MANGANESE ORE.

By ARTHUR HIORNS, Chemist to the Usina Wigg Manganeze Mines, Estacao de Miguel Burnier.

THERE are several solutions from which manganese may be estimated electrolytically, but for the estimation of the metal in the oxide, the acid solution is the most simple, accurate, and rapid. No matter which solution is used, the quantity of manganese in each solution to be electrolysed must be very small, and to obtain accurate results the quantity should never exceed 0.03 gm. of metal.

In the Usina Wigg ore, which has an average of about 55 per cent of metallic manganese, 0.05 gm. of the ore is ample for its proper estimation.

The acid solution is electrolysed hot, and the manganese dioxide which is deposited at the positive pole is converted by ignition to Mn_2O_3 , which gives results varying only in the fourth decimal place.

The solution made strongly acid with nitric acid is contained in a previously weighed platinum dish, and a spiral of platinum wire is brought into contact with the surface of the liquid. The dish and spiral are connected to a Bunsen cell, the dish to the positive pole and the spiral to the negative pole.

The dish is placed on a water-bath, and as soon as the current is started heat is applied to the water-bath and the temperature kept as near 60° C. as possible. It is necessary to have the solution very acid to start with, and as during the operation it is turned into ammonia, a few drops of acid must occasionally be added to it. Great care is necessary to watch that the solution is always acid.

The whole of the manganese is deposited in twelve hours—ten hours seem to be sufficient—but passing the current for twelve hours makes the total deposition

* The amount of WO_3 recovered when the W was precipitated alone was only 0.0980 gm. instead of 0.1256 gm. The great influence exerted by the co-precipitated molybdenum is seen on comparing these results with those previously given (CHEMICAL NEWS, lxxix, p. 64).

certain. The best mode of procedure after the current is stopped is to wash the MnO_2 very carefully with water, then dry it and ignite to convert the MnO_2 into Mn_2O_3 .

The following are the results of the estimation of manganese in two samples of ore by this method. 0.05 gm. of ore taken in each case.

	Weight of Mn_2O_3 . Grm.	Percentage of metallic manganese.
A.		
Electrolysed ten hours	0.0401	57.7800
Electrolysed twelve hours ..	0.0398	57.3500
Electrolysed fourteen hours ..	0.0399	57.4959
B.		
Electrolysed ten hours	0.0374	53.8934
Electrolysed twelve hours ..	0.0376	54.1816
Electrolysed fourteen hours ..	0.0373	53.7493
Average of A	57.5419	per cent
Average of B	53.9414	per cent

The volumetric method of estimation gave in these two cases—

A, 57.5512 per cent. B, 54.0036 per cent.

A CONTRIBUTION TO THE STUDY OF LIQUID MIXTURES OF CONSTANT BOILING-POINT.*

By GARNETT RYLAND.

Introduction.

IN the course of an investigation undertaken for another purpose, a mixture of methyl alcohol and benzene was subjected to a fractional distillation, when it was observed that the larger part boiled like a homogeneous liquid at 57–58°, and could not be separated by repeated distillation with a Hempel tube. By making trial mixtures it was found that, mixed in certain definite proportions, methyl alcohol and benzene will boil to the last drop at 57–57.5°, under atmospheric pressure. If there is present an excess of either of the constituents, the constant boiling mixture and this excess are separated by fractional distillation. As roughly determined, the proper ratio seemed approximately $3\text{CH}_3\text{O} : 2\text{C}_6\text{H}_6$ (38.1 parts of alcohol to 61.9 parts of benzene, by weight).

On examination of the literature no such observation of this mixture could be found, though several similar phenomena are on record.

Historical Sketch.

1. H. E. Roscoe ("On the Composition of Aqueous Acids of Constant Boiling-point," *Journ. Chem. Soc.*, 1861, xlii., 146, and 1862, xv., 270) investigated certain aqueous acids of constant boiling-point which had been regarded as definite hydrates, and found that the proportions of water and acid were not those required by any simple molecular ratio, nor did the composition remain the same when the pressure varied.

Aqueous nitric acid, when distilled under a pressure of 735 m.m., always gave a residue which boiled at 120.5°, and contained 68 per cent of pure acid. Distilled under 75 m.m. pressure, the per cent of pure acid was 66.7, and under 1260 m.m. it became 68.8.

Aqueous solutions of hydrochloric, hydrobromic, and hydriodic acid gave similar phenomena, only in these cases the per cent of acid increased as temperature and pressure decreased. Hydrofluoric acid resembled nitric acid in all respects.

Aqueous formic acid containing 77.5 per cent of pure acid (boiling-point 101.1°) boiled at the fixed temperature

* From the Dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898. The investigation was undertaken at the suggestion of Professor Remsen, and carried on under his supervision. From the *American Chemical Journal*, vol. xxii., No. 5, Nov., 1899.

of $107^{\circ}1'$, under 760 m.m. pressure, the proportion of acid increasing with the pressure.

Aqueous perchloric acid ("On Perchloric Acid and its Hydrates," *Proc. Roy. Soc.*, 1862, xi., 493) gave a residue which boiled constantly at 203° , under atmospheric pressure, and contained 71.6 per cent pure acid.

2. Alexander Bauer ("Ueber eine merkwürdige Erscheinung bei der Destillation eines Gemenges von Bromäthylen und Brompropylen," *Ann. Suppl.-Band.*, 1861, i., p. 250) found that a mixture of ethylene bromide (boiling-point 129°) and propylene bromide (boiling-point 141°) in equivalent amounts, distilled at 134° , and could not be separated by fractionation.

3. J. A. Wanklyn ("Ueber die Destillation von Gemischen; ein Beitrag zur Theorie der fractionierten Destillation," *Liebigs Ann. Chem.*, 1863, xxviii., p. 328) called attention to the fact that in the distillation of a mixture of liquids the proportions in which the constituents pass over depend not merely on their relative quantity and on their respective vapour-tensions at the temperature of ebullition, but also upon their mutual adhesion and on the density of their vapours.

On distilling a mixture of 18 grms. of methyl alcohol (boiling-point 66°) and 17 grms. of methyl iodide (boiling-point 72°), the first third of the distillate contained a greater amount of the less volatile than of the more volatile liquid.

4. Berthelot ("Sur la Distillation des Liquides mélangés," *Ann. Chim. Phys.*, 1864 [4], i., 384) stated that a mixture of 91 parts carbon disulphide (boiling-point 48°) and 9 parts alcohol (boiling-point 78°), by weight, boils at $43-44^{\circ}$, remaining at this temperature from the beginning until the end of the distillation. A mixture of this composition is separated by fractional distillation from an excess of either of its components.

He found the explanation of this phenomenon in essentially physical ideas. If a mixture of two liquids which do not exert any reciprocal action is boiled, both will be volatilised at that temperature at which their united vapour-tensions equal the atmospheric pressure, and in the same ratio by weight as that of the products of their actual vapour-tensions by their vapour-densities respectively. So if the carbon disulphide and alcohol preserved their theoretical vapour-tensions, they would be distilled at about 40° in the proportions of 88.5 parts of carbon disulphide and 11.5 parts of alcohol. But the two liquids exert influence upon each other, as is shown by their mutual solution and by the diminution of the sum of the tensions of their vapours. This influence tends to diminish the individual vapour-tension of each of the liquids, following an unknown law.

5. Ed. Linnemann ("Untersuchung über die Beziehungen des Isopropyl Alcohols zum Propyl Glycol und zum Glycerin," *Liebigs Ann. Chem.*, 1865, cxxvi., p. 40) records three hydrates of isopropyl alcohol (boiling-point $83-84^{\circ}$, 739 m.m.): $3C_3H_7O + 2H_2O$, formed when aqueous propyl alcohol is distilled on the water-bath, boils at $78-80^{\circ}$, 738 m.m., specific gravity 0.832, at 15° ; $2C_3H_7O + H_2O$, formed by dehydration with potassium carbonate, boils at 80° ; $3C_3H_7O + H_2O$, formed by distilling from anhydrous copper sulphate, boils at 81° , specific gravity 0.800.

6. T. E. Thorp ("A Contribution to the Theory of Fractional Distillation," *Fourn. Chem. Soc.*, 1879, xxxv., p. 544) found that a mixture of 1 part methyl alcohol and 3.6 parts carbon tetrachloride boils like a homogeneous liquid about 10° lower than methyl alcohol, the more volatile of the two liquids. Calculation shows that this ratio is almost identical with that obtained by multiplying the vapour-tensions of the two liquids at the temperature of the boiling-point (55.7°) by their respective vapour-densities.

7. D. Konowalow ("Ueber die Dampfspannungen der Flüssigkeitsgemische," *Wied. Ann.*, 1881, xiv., p. 34) investigated the known mixture of propyl alcohol (boiling-point 97.4°) and water in the ratio of about 77:23 parts,

which boils at $85-85.5^{\circ}$. To this composition corresponded the maximum of the curve, whose abscissæ are percentage quantities and ordinates pressures, representing the vapour-tension of the mixture at a specific temperature.

He found also that a 25 per cent solution of butyric acid (boiling-point 163°) in water boiled constantly at 99.5° . Both of these mixtures change their respective proportions on change of the pressure and temperature of distillation.

8. Ramsay and Young ("Note on the Mixture of Propyl Alcohol and Water," *Abstr. Proc. Chem. Soc.*, 1888-1889, p. 101) agreed with Konowalow that the mixture of propyl alcohol and water, thought by Chancel to be $C_3H_7O + H_2O$, which distils to the last drop at 87.5° (738 m.m.), is not a definite hydrate. The normal composition of the mixture (71.46 per cent alcohol to 28.54 per cent water) varied with the pressure under which it was distilled.

Apparatus for Distillation under Reduced Pressure.

Mixtures of methyl alcohol and benzene were distilled under different pressures, and the relative amounts of the two liquids contained in the constant boiling portion of the distillates were determined.

The apparatus used to effect fractional distillation under reduced pressure was arranged as follows* :—

A 250 c.c. separatory funnel was used as a receiver. This was closed with a two-hole rubber stopper, through which passed the adapter and a branched tube, the latter connecting with the manometer, the exhaust, and the pressure regulator. The last was a glass tube about 800 m.m. in length and 20 m.m. in diameter, filled to the necessary height with mercury, and closed at the top with a two-hole rubber stopper through which passed a short and a long piece of small glass tubing. The first connected with the receiver and the latter extended below the surface of the mercury a distance corresponding to the desired diminution of pressure. By this means the pressure could easily be kept constant within 10 m.m. without interrupting the course of distillation. Successive fractions were drawn off from the funnel into an exhausted receiver, through whose stopper the stem of the funnel passed.

The liquid was distilled from a bulb provided with an additional side tube, connected by rubber and a pinch-cock with a small funnel, into which successive fractions were poured. With caution these could be introduced without diminishing the exhaustion.

(To be continued).

NOTES ON

THE ELECTRO-DEPOSITION OF CHROMIUM.†

By SHERARD COWPER-COLES, M.Inst.M.M.

CHROMIUM does not occur in the free state, being generally found as an oxide; its lower oxides closely resembling those of iron, CrO and Cr_2O_3 . Occasionally the metal occurs in a higher state of oxidation, in combination with lead, as plumbic chromate, $PbCrO_4$. It was in this mineral that Vauquelin, in the year 1797, first discovered the existence of chromium.

Chromium forms the colouring matter of several compounds, for instance, the green colour of the emerald, as was shown by Vauquelin; serpentine also owes its colour to chromium. Some of the characteristics of fused chromium are its great hardness (electro-deposited chromium is found to be comparatively soft), its high melting-point, it being more difficult to fuse than platinum, the temperature required being $2000^{\circ}F$.

* My thanks are due to Dr. E. E. Reid, of this laboratory, for his kind assistance in designing and constructing this apparatus.

† Read before the Institution of Mining and Metallurgy, Wednesday, December, 20th 1899.

The following table gives the comparative hardness of electro-deposited chromium, as represented by the number of centigrms. weight on a diamond point, required to produce a scratch:—

	Hardness.
Nickel electro-plate	10.0
Sheffield plate	10.0
Antimony electro-plate	9.0
Palladium (deposited bright)	9.0
Chromium deposited on copper	7.0
Palladium electro-plate	6.6
Cadmium silver alloy, 5Ag, 39.5	5.0
Cadmium (deposited bright)	4.5
Silver (burnished)	4.0
Silver (chemically precipitated)	2.0

Chromium is little affected by nitric acid, even when hot and concentrated, pure chromium oxidising very slowly in hot air, but on heating the surface it becomes readily covered with a thin film of oxide; cold dilute sulphuric acid only attacks it slowly (Roscoe and Schorlemmer).

Some experiments made to determine the relative tarnishing of chromium as compared to other metals gave the following results. The amount of light reflected was determined by means of a Bunsen photometer and two pentane lamps. Highly polished reflectors were coated with various metals, and tested in the photometer, and then placed about 1½ inches from a small arc light for 4½ hours, when readings were again taken, with the following results:—

	Before tarnishing.		After tarnishing.	
	Relative reflecting power.		Relative reflecting power.	
	Unit law.	Square law.	Unit law.	Square law.
Silver (standard)	100	100	—	—
Chromium ..	100	100	56	27
Palladium ..	72	48	47	19
Platinum ..	56	26	44	16
Silver ..	111	105	95	90

Relative Diminution of Reflecting Power, due to Tarnishing.

	Unit law.
Chromium ..	44
Palladium ..	35
Platinum ..	22
Silver ..	10

Professor Hittorf found that chromium in dilute acid solutions in the cold causes hydrogen to be given off, but that chromium is electro-negative to such metals as copper, mercury, and silver. In the same way it fails to reduce such metals from solutions of their neutral salts, and behaves generally as an inert noble metal. On making chromium an anode in cold dilute acids, it dissolves, but not with the formation of chromic or chromous salts: it passes at once into the state of chromic acid. The results of the experiments carried out by Professor Hittorf are thus summarised by him:—Chromium can dissolve electrolytically in any one of its three states, CrO, Cr₂O₃, or CrO₃, according to the nature of the electrolyte and its temperature, its inactive state corresponding, perhaps, with the passive state of iron. The attainment of this passive state is not to be attributed to the presence on the metal of a thin layer of oxide, the hypothesis which is plausible for iron. It appears rather to imply that the surface, at least, of the metal differs in molecular arrangement according to the conditions and surroundings to which it is exposed: in short, that chromium appears to be an allotropic element. Chromium exists in three different states, viz., passive, active, and intermediate, and in each of these states it occupies a different position in the electro-chemical series, and possesses a different chemical behaviour.

Metallic chromium has been obtained by the reduction of oxides and chlorides. Deville made a mixture of chromic oxides and sugar, which he intensely heated in a

lime crucible, or heated chromium sesqui-chloride, with metallic zinc, under a layer of sodium chloride, the metal separating out in glistening scales.

A method of preparing chromium in the electric furnace has been devised by Herr Eschermann, in which a gas-tight steel furnace is used in connection with a movable electrode. A graphite crucible is placed in the furnace, and in this are placed oxide of chromium and sulphide of antimony, in the proportion of 10 to 23. After the furnace is closed, a comparatively small current of from 20 to 23 ampères is passed through the material until melted. Reaction takes place with the development of heat. The resulting mass consists of a regulus of chromium and antimony alloys, whilst the upper part of the crucible has an amorphous mass of antimony oxide, sulphide, &c., adhering to the walls. Every trace of antimony can be removed by repeated meltings, or by powdering and roasting at a white heat. The chromium dissolves a considerable portion of carbon, which separates out as graphite during cooling.

Metallic chromium has lately been obtained in considerable quantities by Dr. Hans Goldsmidt by reducing chromium oxide (Cr₂O₃) with aluminium in a fine state of division, the heat of combination being used for reducing the chromium oxide, the action being started by a small fuse or cartridge composed of peroxide of barium or other suitable per salt, which is fired by a piece of magnesium ribbon to start the reaction. Pure chromium is being made by an electrolytic process by the Electro-chemischen Werke, Bitterfeld, Saxony. Chromium is being sold in Germany at the following prices:—Free from carbon, but containing some iron and traces of silica, 15s. a pound. Chromium free from carbon, and containing 96 per cent chromium, and 3 to 4 per cent iron and traces of silica, at 4s. a pound. Fused chromium is quoted on the American metal market at 7.14 dollars per kilogram., and commercial pure powder at 1.90 dollars per kilogram. Some interesting figures as to the production and value of chrome ore are to be found in the *Mineral Industry* for 1899.

Chromium carbide has been produced by Henri Moissan, the composition being Cr₃C₂ or Cr₄C. Chromium carbide is not acted upon by water; it forms an opaque crystalline mass with a metallic lustre.

Some attention seems to have been recently given to the electro-deposition of chromium from aqueous solutions. The process of Placet Barnet has been worked on a commercial scale. According to the patent specification, the electrolyte is made up by dissolving 100 parts of chromic alum in 100 parts of water by weight, 10 to 15 parts of barium bisulphate. The writer has not obtained deposits from this electrolyte when worked at various temperatures, using carbon and platinum anodes, with current densities varying from 15 to 19 ampères per sq. ft., the voltage at the terminals of the cell being about 4.

Bunsen experimented with the deposition of chromium, and succeeded in getting a good deposit of metal, which had the appearance of iron, but was less alterable in moist air, and even resisted the action of boiling nitric acid, but was acted upon by dilute sulphuric acid and hydrochloric acid.

E. Placet claims to have obtained beautiful deposits of chromium by electrolysis of an aqueous solution of chromic alum, to which he added an alkaline sulphate and a small quantity of sulphuric acid.

The electro-refining of chromium has been tried by the firm of Messrs. Fred. Krupp, Essen, the object being to produce chromium free from carbon, no precautions being taken to prevent the production of a metal containing iron or ferro-chromium. Double chlorides of the metals are used as an electrolyte, the anodes being of ordinary carbonised ferro-chromium, porous diaphragms being used to separate the anode and cathode compartments.

Attempts have been made to deposit chromium alloys, and a patent was obtained in March, 1884. Alloys of chromium were prepared by heating chromium compounds

with charcoal in a closed crucible, and pouring upon the reduced mass $2\frac{1}{2}$ parts of copper, and, subsequently, from 1 to $1\frac{1}{2}$ parts of molten tin, and then granulating, re-fusing, and casting in moulds of the desired forms. The plates thus formed were used as anodes in a solution made by dissolving 1 lb. of cyanide of potassium and 1 lb. of carbonate of ammonia in 1 gallon of water heated to 150° F., until a good deposit was obtained upon the cathode, a low current density being employed.

When a solution of chromium chloride is electrolysed with a negative electrode of mercury, the mercury is found to take up but little chromium, a brownish-black chromium oxide being formed in the liquor. T. Ferec has used with mercury a solution composed of 160 grms. of crystallised chromium chloride, with 100 grms. of concentrated hydrochloric acid, 740 grms. of water, with a current of 22 amperes. In this way he found it possible to obtain $1\frac{1}{2}$ kilos. of solid chromium amalgam in a very short time.

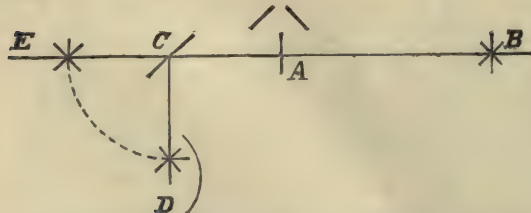
The writer has succeeded in obtaining beautiful bright deposits from a solution composed of chromic chloride 25 parts, water 75. The solution was worked hot at a temperature of 190° F., with a current of between 40 and 50 amperes per square foot. In the cold no deposit of metal was obtained, but a black non-adherent deposit, the voltage at the terminals of the cell being about 4. Gas was evolved at both anode and cathode during the deposition of the metal. Before good deposits could be obtained it was found necessary to add an excess of hydrochloric acid to dissolve the precipitated oxide and form a clear solution.

No deposit of metal could be obtained from a solution composed of chrome alum 100 parts, water 100 parts, barium sulphate 12 parts; the solution was worked hot and cold with current densities varying from 15 to 90 amperes per sq. ft.; a carbon anode and copper cathode were used.

On the table are specimens of electro-deposited chromium; some of the specimens have not been polished, but represent the deposited metal as thrown down on a silvered-copper surface.

The following table gives the actual and comparative amount of light reflected from various electro-deposited metals, including chromium; a Bunsen photometer and standard pentane lamps were used:—

Metals.	Distance from standard light to screen.		Reflecting power.
	Direct light (a).	Reflected light (b).	
		Actual.	$\left(\frac{a}{b}\right) \cdot \left(\frac{a}{b}\right)^2$
	C.m.	C.m.	
Silver ..	69.5	71.5	Actual reflecting powers
Chromium ..	69.5	71.5	
Platinum ..	69.5	97	
Palladium ..	69.5	112	
		Comparative.	
Silver ..	100	Reflecting power.	
Chromium ..	100	" "	$\left(\frac{a}{b}\right)$, taking Ag as 100.
Platinum ..	74	" "	" "
Palladium ..	65	" "	" "



To measure the reflecting power of the various metals, the two standards of light were first compared (E and B) and

the measurements taken. The reflecting surface was then placed in position at C and the lamp at E moved round to D, keeping the length of path of light constant; the lamp B was adjusted and a measurement again made.

ON THE SEPARATION OF FERROCYANIDES FROM CARBONYLFERROCYANIDES, AND THE ESTIMATION OF THESE COMPOUNDS.

By J. A. MULLER.

I. Estimation.

a. Ferrocyanides.—To a solution of ferrocyanide (4 or 5 grms. per litre), slightly acidulated with nitric or acetic acid, nitrate or acetate of lead is added until a precipitate is no longer formed. After twelve hours the precipitate is filtered and washed as thoroughly as possible with boiling water; it is then dried and detached from the filter and treated with an excess of a mixture of 5 volumes of concentrated sulphuric acid and 3 volumes of water. The crucible is covered and heated, at first gently, on a sand-bath, then more strongly until the excess of sulphuric acid is driven off. The crucible is then placed in a muffle, and gradually heated to dull (not bright), redness; it is kept for some time at this temperature, then allowed to cool, and the residue, formed of a mixture of sulphate of lead and ferric oxide, is weighed. The filter, still impregnated with the precipitate, is treated in the same manner, and the weight of this residue is added to the first weight. In this second treatment care must be taken to moisten the residue with sulphuric acid after the preliminary heating, it is then calcined afresh.

The weight of the mixture of sulphate of lead and ferric oxide multiplied by 0.5378 gives that of the corresponding ferrocyanide of potassium.

By proceeding in this manner, I found in nitric solution 99.72 per cent, and in acetic solution 100.20 per cent.

b. Carbonylferrocyanides.—To the dilute solution acidulated with acetic acid, an excess of pure acetate of copper is added after twenty-four hours, filter, and wash thoroughly; this operation takes a very long time. The precipitate, with the filter, is then placed in a large platinum crucible, and moistened with a mixture of sulphuric acid and water of the strength previously given; the crucible is covered and heated, at first very gently on a sand-bath, then more strongly to redness, so as to completely burn the carbon. The residue is dissolved in fuming hydrochloric acid, and from the previously diluted solution the copper is precipitated in the form of cupric sulphide, which is transformed, after desiccation, into cuprous sulphide by Rose's method.

The weight of Cu_2S , multiplied by 2.787, gives the weight of the corresponding carbonylferrocyanide of potassium.

By experiment I found 99.12 per cent.

II. Separation.

In a solution of pure carbonylferrocyanide of potassium, slightly acidulated with acetic acid, acetate of lead forms no precipitate, while the ferrocyanide is completely precipitated, as has been shown above in the state of ferrocyanide of lead.

But if the solution of the prussiate contains carbonylferrocyanide as well, the precipitate of ferrocyanide of lead formed contains a notable quantity of carbonylferrocyanide of lead.

The following is the way in which, after a large number of experiments, I succeeded in totally separating the two ferrocyanides:—

* The liquid does not pass clear until the filter is impregnated with the precipitate; the filtration is therefore excessively slow.

To the weak solution of the ferrocyanides (4 to 5 grms. per litre), slightly acidulated with acetic acid (8 to 10 grms. per litre), is gradually added, while stirring, a slight excess of a solution of acetate of lead; the mixture is then left in the dark until the supernatant liquid becomes clear; this takes from one to two days. The clear liquid is then decanted carefully with the aid of a pipette, and filtered several times until it is quite limpid; an excess of acetate of copper is then added for the purpose of precipitating the carbonylhydroferrocyanic acid in the state of a cupric salt. As for the plumbic precipitate, it is dissolved in a slight excess of a solution of pure soda, and the mixture is poured, while still stirring, into water containing enough acetic acid for the whole to be still acid after the addition of the liquid. After having washed the beaker containing the sodic solution with acidulated water, and adding the washings to the principal solution, the plumbic precipitate re-forms; when this latter is completely deposited it is left in the dark for twenty-four hours.

The above series of manipulations is then repeated, once not being sufficient.

After having made three successive solutions and precipitations of the plumbic precipitate, the latter is thoroughly washed and estimated as was described in *a*. As for the liquids separated after each precipitation and addition of acetate of copper, they are filtered, and the precipitate of carbonylferrocyanide of copper, after being well washed, is treated as in *b*.

By operating exactly as has just been described a mixture composed of—

K_4FeCN_6	0.7348 grm.
$K_3FeCOCN_5$	0.6244 "
gave me—	
K_4FeCN_6	0.7302 "
$K_3FeCOCN_5$	0.6267 "

that is 99.37 per cent of the first salt, and 100.37 per cent of the second.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 10.

THE PREPARATION OF PURE ALKALINE NITRITES.

By E. DIVERS.

NITRIC acid is made to react on starch, or on arsenious acid; the temperature and the strength of the acid are regulated in such a manner that in the products obtained nitric oxide should be in excess over the peroxide. The gas is passed into an empty flask, where the nitric acid is deposited, then into a concentrated solution of a pure alkaline hydrate or carbonate.

The nitrites of potassium and sodium are slightly yellow, very soluble in water, and give solutions alkaline to litmus. When free from nitrates their solutions may be evaporated to dryness without decomposition. The two salts when crystallised are anhydrous, but they soon deliquesce. Nitrite of sodium melts at 271° .—*Journ. Coll. Sci., Tokio, Japan*,

THE FORMATION OF HYPOCHLORITES AND CHLORATES.

By F. FÖRSTER and F. JORRE.

THE authors describe a large number of experiments made with a view to the study of the formation of chlorates by the action of chlorine on the alkalis. The results of their researches agree generally with those of Lunge and Landolt (*Journ. Soc. Chim. Ind.*, 1885, p. 722), who studied the conditions under which the transformation of hypochlorite of lime in chlorate took place.

The classic equations which are supposed to represent the action of chlorine on caustic potash do not conform with the true facts of the case. When chlorine is passed through alkaline solutions, until they contain an excess, the chlorate is formed rapidly. The theory, according to which the chlorates should be formed more easily by passing the chlorine through warm concentrated solutions is incorrect. The addition of an acid to solutions of hypochlorite of varying strengths helps the formation of chlorates; the explanation of this fact is found in the theory of electrolytic dissociation.

It has also been found that, while solutions of hypochlorite and hypochlorous acid are stable when isolated, they, on the contrary, react on one another when mixed; the transformation into chlorate is rapid and complete.

As far as the electrolysis of solutions of chloride of lime containing chloride of potassium or sodium is concerned, the authors confirm the observations of Ostel; thick crusts, which gradually become detached, separate from the cathode, and free chlorine is given off.—*Journ. für Prakt. Chem.*, 1899, p. 53.

ON THE ANALYSIS OF MANUFACTURED INDIARUBBER.

By Dr. R. HENRIQUES.

DURING the years 1892, 1893, and 1894, I published the results of a research undertaken with the object of establishing analytical methods applicable to the treatment of manufactured indiarubber (*Moniteur Scientifique*, August, 1894, p. 617). The methods I then described have as a rule proved of practical value, not only in my own laboratory, but also in the hands of a certain number of colleagues employed in this industry. With practice I have since been able to simplify certain of these methods, and I now think the time has arrived for publishing the results obtained since the publication of my first papers.

I. Estimation of the Total Sulphur and the Mineral Constituents.

The method finally adopted is as follows:—A hemispherical porcelain crucible, about 6 c.m. in diameter, and of about 30 c.c. capacity, is covered with a watch-glass, allowing room for a glass stirring rod. This crucible is filled to about one-third, that is to say, with about 10 c.c., of pure concentrated nitric acid, and heated gently on a water-bath. One grm. of the finely divided sample is weighed out, and gradually added to the acid. The reaction soon commences with the disengagement of reddish fumes. This must be regulated by adding fresh portions of the substance in such quantities that the reaction keeps lively without getting too strong.

This can easily be done by either removing the crucible from the water-bath, re-heating, if necessary, and varying the quantity of the substance added. When the attack is finished the heating is continued until the disaggregation is complete. There is now no longer any loss to be feared by projection; the watch-glass can therefore be removed and wiped with a filter paper, which is placed in the crucible, and the evaporation is continued until the liquid takes a syrupy consistency. 20 c.c. of acid are then added, and the concentration repeated and carried as far as possible so as to drive off all excess of acid.

There now remains, to entirely destroy the organic matter. For this purpose we add to the syrupy extract a suitable dose of a mixture of dry soda (5 parts) and salt-petre (3 parts), and knead it well with the stirring rod so as to form an apparently dry powder. This is then covered with a layer of the mixture of soda and salt-petre, of which about 5 grms. is required altogether, and left on the water-bath until no more carbonic acid gas is given off. To prevent all chance of deflagration, which might

lead to losses, the calcination should be conducted very carefully. The crucible must be placed over a very small flame, which must be increased very gradually after some minutes, after having covered the crucible with another similar one so as to form a dome over it. If by chance the combustion becomes too fierce at any moment the projections will be stopped by the cover, and the substance thus caught must be melted apart, with a fresh dose of the oxidising mixture.

Under ordinary circumstances the mass gradually becomes black from the edges towards the centre, and only gives off empyreumatic fumes, which condense in the covering crucible, forming brown stains absolutely free from sulphur.

The first calcination once completed, the cover may be removed, and the substance heated to fusion, which can be accelerated by stirring with the glass rod. The entire operation of fusing requires from an hour to an hour and a-half. With a little practice it is easy to prevent any loss by deflagration. As a further precaution, it is as well, besides the careful regulation of the calcination, to use a very homogeneous mixture of soda and saltpetre, passed through a fine sieve, and thoroughly mixed with the nitric extract.

When the calcination is conducted without any deflagration, the same crucible can be made to serve for several operations. After cooling, the mass is taken up with boiling water and thrown on a filter. The whole of the sulphur in the sample will be found in the solution in the form of sulphate, and the metals remain on the filter in the form of oxides or carbonates, with the silica; it is only when this latter is present in considerable quantities that a part of it will be found in the solution. The solution is acidulated with hydrochloric acid, evaporated to dryness on the water-bath, taken up with concentrated hydrochloric acid, the silica separated, and sulphate of barium precipitated in the usual manner.

The metallic oxides are taken up on the filter with warm hydrochloric acid, which leaves the silica only insoluble. In the hydrochloric solution the metallic oxides are estimated in the ordinary way.

When mercury is among the constituents of indiarubber—in the form of cinnabar, for example, it is often met with in dental rubbers—it must be estimated separately by attacking with nitric acid, diluting with water, filtering and precipitating with sulphuretted hydrogen.

Cinnabar is not such a rare constituent of indiarubber as might be supposed. Besides dental rubbers it is met with in certain fine hardened rubbers (stabilite), and in small quantities in many red rubbers, where it is associated with vermilion or golden sulphide of antimony, or even with oxide of iron, the colour of which it modifies to a certain extent.

II. Estimation of Factitious Matter in Vulcanised Indiarubbers.

The method previously described (*Moniteur Scientifique*, August, 1894, p. 617) has not been appreciably modified. Although it is rather long we have not succeeded in shortening the time occupied without interfering with its exactness. The only modification which has been introduced consists in the following, that instead of collecting the rubber exhausted with alcoholic potash on a tared filter, for the purpose of weighing by difference, we simply use any filter, from which the material becomes detached with the greatest ease during the drying in the oven. The complete desiccation is then effected separately and the weighing done direct.

III. Estimation of Non-saponifiable Oils in Vulcanised Mixtures.

The non-saponifiable oils, mineral oils, resin, and paraffin are often met with in commercial rubber, not only because the manufacturer adds a certain proportion to render the re-heating and cutting more easy, but also

because several factitious rubbers and most regenerated or devulcanised rubbers contain them in notable proportions.

The estimation of these bodies is effected at the same time as that of the factitious matter. After treating the sample with alcoholic potash and weighing the residue, the latter is taken up by several applications of ether, which easily and completely dissolves all the non-saponifiable oils. The sample is simply ground with ether in a mortar and decanted, the rubber remaining well agglomerated. This extraction is continued as long as the solvent becomes coloured; the sample is then dried again, and the difference in weight is taken as non-saponifiable oil. It is on the residue from this extraction that the estimation of the combined sulphur and ash is effected, for the calculation of the approximate proportion of factitious matter present.

IV. Estimation of Factitious Matter in Non-vulcanised Indiarubbers.

The method of estimating factitious matter, such as already described (*loc. cit.*), gives very concordant results in the analysis of commercial vulcanised rubbers. It is applicable equally to the analysis of blocks or sheets of patent rubber, cut or otherwise, but it cannot be applied without modification to raw cut rubbers, that is to say, to mixtures prepared for vulcanisation.

Even after four hours boiling with alcoholic soda, the factitious matter is not entirely dissolved, and on repeating the extraction a fresh loss of weight is observed, which, however, does not even then correspond to the total amount of factitious matter contained in the mixture. As we already know that the factitious matter is entirely soluble in alcoholic soda and that the rubber itself is not soluble at all, this result can only be attributed to mechanical action, the thickness of the pieces preventing the interior layers from being reached by the solvent. To remove this difficulty I operated as follows:—

Five grms. of the material were placed in an Erlenmeyer flask, in contact with 25 c.c. of benzene. This was heated for an hour on a water-bath, after fitting a vertical condenser, and left to macerate for a night. The mass is by this time converted into a thick glue, to which is added 25 c.c. of normal alcoholic soda solution. After boiling again in the same manner for four hours, and then distilling off the solvents, the residue is taken up with boiling water. The whole is placed in a crucible, treated several times with water, and the coagulum of rubber separated. Filtering is useless, and the whole material is collected in a pasty mass, which is ground in a mortar with boiling water until all alkaline reaction disappears.

The proof that under these conditions the elimination of the factitious matter is complete, is furnished by the analysis of the remaining rubber, which does not contain a trace of sulphur. Further, a second extraction, conducted in the same manner, gives no supplementary loss of weight. The results of three analyses agree to within 1 per cent.

V. Estimation of Non-saponifiable Oils in Non-vulcanised Rubbers.

With non-vulcanised rubbers it is impossible to apply the method of estimation of non-saponifiable matter, described in paragraph III., on account of the partial solubility of the indiarubber itself in ether. In this case we make use of acetone, with which the rubber, freed from factitious matter and free sulphur, is boiled as in paragraphs II. and IV. The extraction by boiling is continued until the solvent is no longer coloured. The rubber then remains in a pasty gluey state, which is very difficult to dry for the purpose of weighing. Further, it is preferable to weigh the dissolved material direct; for this purpose the acetone extracts are filtered hot in a matrass, and after distilling off the acetone the residue is taken up with a little ether and left to evaporate spontaneously after filtration; the residue is then dried in the oven at 100° and weighed.

Cold acetone does not easily dissolve the non-saponifiable substances met with in indiarubbers; but on boiling they are dissolved quite sufficiently to enable the total extraction to be accomplished without difficulty.

VI. Estimation of Carbonic Acid.

Carbonates are frequently used in the manufacture of indiarubber, particularly chalk and carbonate of magnesia, but we also occasionally meet with ceruse and carbonate of zinc (?). As, on the other hand, the oxides corresponding to these carbonates are often met with, it is interesting, in certain cases, to estimate the carbonic acid exactly. For this purpose a Geissler apparatus is used according to the directions given by Fresenius. It is essential that the rubber analysed should be of extreme fineness, and further—as vulcanised indiarubbers may contain sulphides, either through their being added, as in lithopone, or through their formation during the vulcanisation, by the action of sulphur on the metallic oxides—care must be taken that the carbonic acid gas given off does not carry with it any sulphuretted hydrogen.

For this purpose it suffices to replace the water with which the apparatus is charged, with a dilute solution of sulphate of copper. The carbonic acid gas which is then given off is entirely free from sulphuretted hydrogen.

This method, when used for the analysis of a non-vulcanised rubber, only gives bad results. In such a case, no matter how finely the sample may be divided, the hydrochloric acid is unable to reach the whole of the carbonate which is protected by the rubber; the attack, therefore, remains superficial. It is then necessary to have recourse to the preliminary extraction of the sample with nitrobenzene as proposed by O. Weber (CHEMICAL NEWS, Jan. 5, 1900, p. 5).

We operate on a few grms. of material which are boiled with nitrobenzene; the material is then washed with benzene, collected on a filter, dried, weighed, and an aliquot part taken for the estimation of the carbonic acid. The attack of the substance, which has now become pulverulent, is very rapid.

I might here remark that I have not, on many occasions, been able to obtain satisfactory results when following the method proposed by Weber, either in its original form or in the improved form which he has since devised. Non-vulcanised, or slightly vulcanised rubber, it is true, dissolves in boiling nitrobenzene, but if we have to deal with hard or highly charged rubbers it is very difficult to dissolve the whole of the gum, and the filtration of the residue presents insurmountable difficulties.—*Zeitschrift für Angewandte Chemie*, 1899, p. 802.

JUVENILE LECTURES.

At the Society of Arts, on Wednesday evening, 3rd inst., Mr. HERBERT JACKSON delivered the first lecture of his course addressed to a juvenile audience, the subject being "The Phenomena of Phosphorescence."

The lecturer commenced by a reference to the natural sources of phosphorescence as seen in the sea and in some cases of animal decay, &c. Phosphorescence and fluorescence might be treated as identical terms. They were illustrated by the exhibition of a phosphorescent jet of steam from a vessel containing water and phosphorus, and of the effect produced by sprinkling fluor-spar on a heated plate. He then proceeded to show how there were certain substances which showed light, generally of a yellowish or greenish colour, when exposed to the more refrangible rays,—the rays at the violet end of the spectrum,—and showed how the visible spectrum was apparently extended in length when the violet and ultra violet rays fell on a surface prepared with such materials as sulphate of quinine or thallene. On passing a slab of uranium glass along the spectrum, it was made manifest that no effect was produced on the glass by the red end,

whereas as soon as it was placed in the violet rays it glowed with its characteristic greenish yellow colour. The phosphorescence of quinine and of fluorescein when the solution was dropped into a tall jar of water was also shown, and further illustrated by burning sulphur in oxygen in a jar immersed within a larger jar filled with the phosphorescent solution. The phosphorescence of such materials only lasted while the exciting cause was present, but there were other materials which continued to emit light after the exciting light had been withdrawn; of these possibly the best known was Balmain's luminous paint. A card coated with this was exhibited, and it was shown how the brightness of the phosphorescence was temporarily increased by heat and diminished by cold. It was, however, possible to make other similar substances which acted in the same way, but showed light of different colours, and Mr. Jackson exhibited a fine series of phosphorescent bodies, principally lime salts, which, when excited by the brilliant discharge from a large induction coil, glowed for a certain time with various tints, blue, yellowish green, and pinkish red. Phosphorescence could be produced in a block of lime, such as that used for the lime-light, but it was of very short duration. If, however, such a block were rapidly rotated in the close neighbourhood of the induction discharge, the phosphorescence produced by the discharge lasted long enough to be perceived on the side of the lime turned away from the spark as it rotated. After this the lecturer passed to the phosphorescent effects produced by the electrical discharge in vacuum tubes, and showed the very beautiful results in a long tube, in which a spark from an induction-coil was passed, as the air and the various gases with which the tube was filled were gradually exhausted.

NOTICES OF BOOKS.

The Cost of Living as Modified by Sanitary Science. By ELLEN H. RICHARDS. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1899. 124 pp. 12mo. Cloth.

MRS. ROBERT H. RICHARDS, Instructor in Sanitary Chemistry in the Massachusetts Institute of Technology, Boston, is already known to thoughtful housewives by her works on the "Chemistry of Cooking and Cleaning," and on "Food Materials and their Adulterations." In the present volume she discusses the prime economic problem of households, how to secure comfort, health, and rational pleasure for the family, to the greatest financial advantage, in the light of modern sanitary science. She writes especially for those who earn small salaries, say from fifteen hundred to three thousand dollars a year (£300 to £600), and whose station in life causes them to make greater expenditures than their incomes warrant; she believes that the problem is more difficult for them than for day labourers and artisans earning but six hundred dollars a year (£125), and whose aspirations are far smaller.

The book discusses Standards of Living, Household Expenditure, and its ideal division among certain departments; Food; Clothing in relation to Health; Emotional and Intellectual Life, and the Organisation of the Household.

Under Food the author makes an apt citation from a writer of antiquity: "Wherefore do you spend money for that which is not bread, and your labour for that which satisfieth not?" (Isaiah, lv., 2).

Mrs. Richards says: "Let not woman grasp for the reins of business until she can master the running of one home." That the household is not run on economic principles is acknowledged by all, and the author thinks that the "women's province is degraded by her own connivance, since knowledge is at her disposal and she does not avail herself of it."

This suggests the question how can such useful books as this one, for example, be brought to the attention of those housewives who most need them? The shiftless, ignorant, yet proud woman who thinks she knows it all, is the very one who can scarcely be induced to examine a thoughtful, economic treatise on the "Cost of Living," while the graduate of a woman's college, or it may be of a University, accustomed to serious study, will read, ponder, and profit. Mrs. Richards is, however, altruistic and thinks the outlook full of hope.

The volume is pleasantly written, free from technicalities, and can be easily "understood of the common people."

H. C. B.

Methods for the Analyses of Ores, Pig-Iron, and Steel; in use at the Laboratories of Iron and Steel-works in the Region about Pittsburg, Pa., Contributed by the Chemists in charge, and Edited by a Committee of the Chemical Section, Engineers' Society of Western Pennsylvania. Eastoe, Pa. : Chemical Publishing Co. 1898. Pp. 133.

THE methods of analysis described in this volume were originally published in the year 1896, by the Engineers' Society of Western Pennsylvania, but, as the supply of copies became exhausted, the present publication, in a more convenient form, has been undertaken by the Chemical Publishing Company.

There are here described the methods used in sixteen different laboratories, and they will be of the greatest interest to all practical chemists engaged in this branch of chemical analysis. There is also an Appendix containing various special methods of analysis of ores and furnace products, the whole forming a valuable collection which will make a useful addition to the book-shelf.

Chemistry for Organised Schools of Science. By S. PARRISH, B.Sc., A.R.C.S. (Lond.). With an Introduction by D. FORSYTH, M.A., D.Sc. London: Macmillan and Co., Ltd. 1899. Pp. 262.

THE method of treatment adopted in this book follows, to a great extent, that employed in the two years' course in Chemistry in the School of Science in the Leeds Higher Grade School, and the author has found that the order adopted is both reasonable and practical. We are glad to see that the balance is brought into practical use early in the course, instead of—as is so often the case—being left till towards the end. The fundamental principles and practice of chemical analysis can soon be acquired by an ordinarily intelligent student, and, in our opinion, the sooner he learns the use of the balance the better.

In the second year the greater proportion of the experiments are quantitative, while symbols, theory, and formulæ are introduced about the middle of the course.

The whole book seems to be well arranged and written, while the illustrations are numerous and instructive. We feel sure that students will find it of great service, as by its help much work can be done in the absence of a teacher. At the end of the book will be found a number of examination questions and exercises, and a good index.

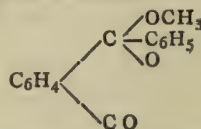
The Goldsmiths' Institute, New Cross, S.E.—Chairman of Governors: The Prime Warden of the Worshipful Company of Goldsmiths.—A course of fifteen lectures on Third Year Organic Chemistry will be given on Friday evenings, at 8.30, by William Jackson Pope, F.I.C., F.C.S., F.M.S., F.C.G.I., commencing on January 19th, 1900. In this course of lectures particular attention will be paid to the discussion of recent work and current views relating to organic chemistry. The lectures are suitable for advanced students preparing for the Organic Chemistry Examinations in Honours of the London University and Science and Art Department. Fee for the course, 5s.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 26, December 26, 1899.

Researches on the Tautomerism of Benzoylbenzoic Acid.—A. Haller and A. Guyot.—Whatever the method used for the preparation of benzoylbenzoic acid the authors always obtain the same ether, crystallising in prisms melting at 52°. One of the methods employed excludes, to a great extent, the existence of a lactic form of the benzoylbenzoic compound. The conclusion is then drawn that the two forms of the ether do not exist, and that only the form $C_6H_4 \begin{smallmatrix} \diagup COC_6H_5 \\ \diagdown COCH_3 \end{smallmatrix}$ is susceptible of being prepared, the second form—



being unstable and quickly transposed into the other form.

The Temperature of Transformation of the Two Varieties of Mercuric Iodide.—D. Gernez.—The transformation of red quadratic mercuric iodide into orthorhombic yellow crystals, under the influence of heat, is a reversible reaction, but the phenomenon presents, in both cases, a retardation: (1) due to what may be called "crystalline surfusion," and which shows itself when the yellow iodide is slowly cooled to a lower temperature to that at which the transformation can be effected. This retardation may persist for some time. (2) The reverse of the last, the red crystals persisting at a temperature higher than that at which they can exist in the yellow variety. These phenomena explain the diversity of the various numbers previously given. The author discusses the theoretical explanation of the above two phenomena.

New Experiments on the Activity of Manganese with respect to the Phosphorescence of Strontium Sulphide.—José Rodriguez Mourelle.—In a previous paper the author described the result obtained in the preparation of phosphorescent strontium sulphide, by substituting, as the active material, bismuth subnitrate or manganese carbonate in very small quantities. The phosphorescence, though always intense, presents in this case a very clear yellowish green colouration. By varying the experimental conditions the author arrives at the conclusion that freshly prepared carbonate of manganese, precipitated and quite dry, and kept from contact with air, seems to possess the active power to the greatest degree.

Silicide of Molybdenum.—E. Vigouroux.—Molybdenum prepared by M. Moissan's method in the electric furnace will unite directly with silicon. The substance formed, of which the composition is analogous to tungsten silicide, shows almost identically the same properties. It burns with incandescence in chlorine at about 300°, forming tetrachloride of silicon and black molybdenum perchloride which is deposited in the apparatus.

Molybdenum Bisulphide.—Marcel Guichard.—No previous method allows of the preparation of tolerably large quantities of pure molybdenum bisulphide. After several trials the author found two satisfactory preparations, the one giving crystalline and the other amorphous bisulphide. Both methods are described in detail and analysis given.

Action of Nitrous Acid on the Leucobase $C_{18}H_{24}N_2$.—A. Trillat.—Nitrous acid is allowed to act on an acidulated solution of the base $C_{18}H_{24}N_2$; a very

vigorous action then takes place. The compound resulting from this action is in the form of yellow needles, sometimes several c.c. long, which melt at 163° — 164° . They are soluble in hot acetic acid, hydrochloric acid, and alcohol, but insoluble in water. This substance has been identified with paranitrodimethylaniline,



Heat of Neutralisation and Acidimetry of Cacydic Acid.—Henri Imbert.—The author's experiments show that cacydic acid is a feeble monobasic acid, and as it differs in reality from dimethylphosphoric acid, not only by the substitution of arsenic for phosphorus, but also by having two atoms of oxygen less. We see also that the presence or absence of oxygen in the molecule increases or diminishes the degree of energy of the acid function, since dialcylphosphoric acids are acids which are strongly neutralisable by the same quantity of the base of helianthine and phthalein.

The Hydrate of Sodium Peroxide and the Preparation of Hydrogen Peroxide.—M. de Forcrand.—Vernon Harcourt discovered a crystallised hydrate of sodium, $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, which was formed by the slow evaporation of aqueous solutions of Na_2O_3 . The author continues this research, but finds a better method of preparation from a concentrated solution of Na_2O_2 . The solution being made at 0° , and the temperature gradually raised to about 40° , on again cooling it to 0° an abundant crop of crystals separate out. No definite formula has been found for these crystals. The author also determined the heat of solution of this hydrate.

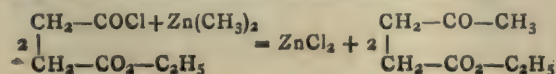
Anhydrous Sesquichlorides of Rhodium and Iridium.—E. Leidié.—The difficulty of preparing these substances by the direct action of chlorine on the metal has led the author to devise an indirect method for their preparation. Rh_2Cl_6 is most easily prepared by heating in a current of pure dry chlorine to 400° one of the three double chlorides of potassium, sodium, or ammonium, which have been dried at 100° — 105° . Ir_2Cl_6 is obtained by heating the dry double salt $\text{Ir}_2\text{Cl}_6 \cdot 6\text{NH}_4\text{Cl}$ in chlorine gas to 440° .

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 14.

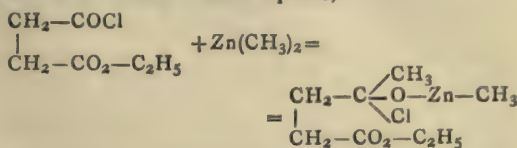
General Method for the Synthesis of the Ketonic Acids.—E. E. Blaise.—None of the methods at present known lend themselves to the synthesis of the ketonic acids of the form $\text{CH}_3\text{---CO---C(R)}_2 \dots \text{---CO}_2\text{H}$. Now the dimethyllevulic and dimethylhexanonioic acids, which are derived respectively from the oxidation of campholene and β -campholenic acid, belong to this type; the author has therefore sought for a new method for effecting their synthesis. The method adopted is based on the action of zinc-methyl on the chlorinised ethers of the bibasic acids,—
 $2\text{COCl---C(R)}_2 \dots \text{---CO}_2\text{R} + \text{Zn}(\text{CH}_3)_2 =$
 $= \text{ZnCl}_2 + 2\text{CH}_3\text{---CO---C(R)}_2 \dots \text{---CO}_2\text{R}.$

To obtain a pure chlorinised ether it is necessary to treat the corresponding ether acid with trichloride of phosphorus at the lowest possible temperature, and to be careful not to submit the product of the reaction to distillation, which would entirely change its composition.

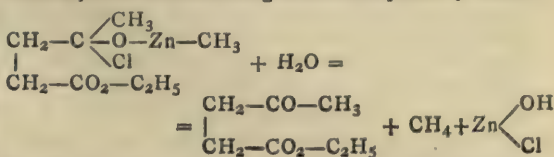
A New Synthesis of Levulic Acid.—E. E. Blaise.—This synthesis has been effected by the action of zinc-methyl on the chlorinised succinic ether. The manner in which this reaction is carried out has a great influence on the return obtained. On the one hand, not more than half a molecule of the metallo-organic compound may be employed for each molecule of the chlorinised ether—



Or, on the contrary, equal molecules may be taken and the reaction limited to its first phase,—

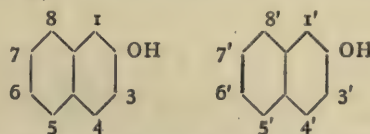


the compound obtained being then decomposed by water,—

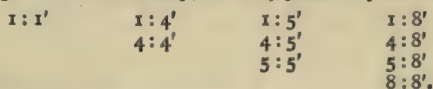


Again, we can pour the zinc-methyl into the chlorinised ether, and proceed in the inverse sense. Experience has shown that the best returns are obtained by using equal molecules of chlorinised ether and zinc-methyl, and in pouring the first into the second, in such a manner that there will always be an excess of the metallo-organic derivative present. The author has also applied this method to dimethylsuccinic and dimethylglutaric acids for effecting the synthesis of dimethyllevulic and dimethylhexanonioic acids,

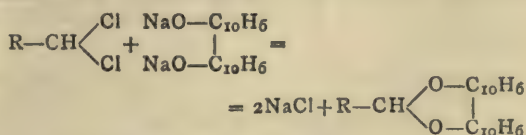
The Constitution of β -Binaphtylol.—R. Fosse.—The number of binaphtylols foreseen theoretically is 28, the union of the two molecules taking place in the positions $\alpha\alpha$, $\beta\beta$, or $\alpha\beta$. The binaphtylol obtained by the author is a derivative of $\alpha\alpha$ -binaphtyl; in fact, $\alpha\alpha$ -binaphtyl is obtained by distilling binaphtylol with zinc powder. If we call the carbon atoms of one molecule of naphtylol 1, 3, 4, . . . 8, and the atoms of another molecule 1', 3', 4', . . . 8',—



the junction can only take place between 1, 4, 5, 8, and 1', 4', 5', 8',—that is to say, the only possible junctions are



Action of the Aldehyds and the Aldehydic Chlorides on Binaphtylol Acetals.—R. Fosse.—The author has reacted with aldehydic chloride on sodic binaphtylolate with perfect success, the reaction being expressed thus:—



By an analogous method Tawildarow prepared ordinary acetal by reacting with bromide of ethylidene on ethylate of sodium.

On some New Derivatives of β -Binaphtylol.—R. Fosse.—The author describes the method of preparing and the composition and properties of several new derivatives of β -binaphtylol, among which are di-propionate of binaphtyl, $\text{C}_{26}\text{H}_{22}\text{O}_4$; di-butyrate of binaphtyl, $\text{C}_{28}\text{H}_{26}\text{O}_4$; phthalate of binaphtyl, $\text{C}_{28}\text{H}_{16}\text{O}_4$; bromobinaphtylol, $\text{C}_{20}\text{H}_{12}\text{Br}_2\text{O}_2$, &c.

On the Symmetrical Dinitro-ditolylcarbamides.—H. Vittenet.—The author has prepared the nitrated di-

tolyl carbamides by two methods, by which he has already previously obtained the substituted diphenylcarbamides: 1st, he reacted with the nitrotoluidines on COCl_2 in a 20 per cent solution in toluene, and 2nd, he reacted with the same bases on $\text{CO} \begin{smallmatrix} \text{O} \\ \diagup \text{C}_6\text{H}_5 \\ \diagdown \text{O} \end{smallmatrix}$. The method with phosgene gave good returns, but with carbonate of phenyl he got much lower returns and far less pure products. In this paper he fully describes these nitrotolyl carbamides, as well as the bases formed by their reduction.

Some Cuprous Phenylhydrazinic Salts.—J. Moitiesier.—Phenylhydrazine forms, with cuprous chloride, bromide, and iodide, crystallised compounds analogous to those formed by ammonia, aniline, and pyridine. The cuprous phenylhydrazinic salts are almost insoluble in cold water, soluble in solutions of hyposulphite of soda, insoluble in alcohol and ether, which remove the phenylhydrazine. They gradually decompose in air, especially in moist air, as they also do very rapidly at a high temperature.

On the Aloïnes.—E. Léger.—The author states that all the aloïnes, with the exception of *nataloïn*, such as *socaloïn*, *barbaloïn*, *curacaloïn*, *zanaloïn*, have the same centesimal composition; the differences noticed are principally those of colour and the quantity of water of crystallisation contained in the aloïnes and their derivatives.

On Barbaloïn.—E. Léger.—The study of the derivatives of barbaloïn has confirmed the author's opinion that barbaloïn should be represented by the formula $\text{C}_{16}\text{H}_{16}\text{O}_7$, and that it contains 3OH.

The Solubility of the Proteoses and the Peptones in Alcohol.—Dr. J. Effront.—The author finds that the true peptone in the commercial article is soluble in alcohol, while the insoluble part, or that portion which is precipitated by sulphate of zinc, consists principally of the proteoses; he also establishes the point that the solubility of the proteoses depends on the reactions of the medium employed.

On the Estimation of Albumoses and Peptones.—Dr. J. Effront.—The author fully describes his method for the estimation of albumoses and peptones, which is based on the determination of the syntonin. In neutral solutions the albumoses are precipitated by alcohol, while the peptones go into solution.

On the Dissolving Power of Pepsine.—Dr. J. Effront.—Pepsine, like amylose, has a dissolving as well as a hydrating power. These distinct properties of pepsine have not yet been examined separately; the author has therefore thought it of interest to carry this out, and he here, in a rather long paper, gives the results of his experiments with acids, alkalis, chlorides, sulphates, and a number of other chemical substances; he finds that sulphates particularly have a very strong retarding action.

The Chemical Analysis of Rocks. Estimation of Potassium and Sodium.—E. Bonjean.—Already inserted in full.

MISCELLANEOUS

Cornell University Laboratory.—A new addition to the chemical laboratory at the Cornell University has recently been built at a cost of 55,000 dollars. It is intended for the accommodation of the divisions of Inorganic Chemistry and Physical Chemistry, and also to relieve the overcrowding in the old laboratory. The new building is 130 feet long by 65 feet wide, of most substantial build, and thoroughly equipped with apparatus and fittings of the highest class. The sub-basement, basement, and first floor are occupied by the division of Inorganic Chemistry, and the second floor by Physical Chemistry.

At the end of the building on the basement floor is the assay laboratory, provided with seven crucible furnaces, five muffle furnaces, one gas assay furnace, and one powerful gas blast furnace; it is situated immediately above the ore-storage room; the adjoining rooms are arranged—one for gold and silver assaying, and one as a balance room. The last room is fitted with an electric furnace for chemical experiments where the electric arc is used as a source of heat. On the first floor there are—the private laboratory for the Professor of Chemistry, and two small rooms thoroughly equipped for research. These are each intended for the use of one student only. On the same floor are found the museum, the laboratory for spectroscopic work, and the lecture room. The whole of the second floor is devoted to physical chemistry, such as electro-chemistry, &c. The opportunities now offered by the Cornell University for the study of Physical Chemistry are, says Professor Bancroft, quite unequalled in the United States, and the equipment will bear comparison with that of the Leipsic laboratory, especially when one takes into account the fact that constant temperature rooms, spectroscopic laboratories, electric furnaces, &c., are available on the floors of the building assigned to inorganic chemistry.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.

WEDNESDAY, 17th.—Society of Arts, 8. "Ventilation without Draughts," by Arthur Rigg.
— Microscopical, 8. President's Address.
— Institution of Mining and Metallurgy, 8. "A Development in Gravitation Stamp Mills," by D. B. Morison and D. A. Bremner.
"Notes on Gold and Platinum Mining in the Ural Mountains," by D. A. Louis, F.I.C.

THURSDAY, 18th.—Chemical, 8. "Nitrogen Halogen Compounds," by Julius Stieglitz and E. E. Slosson. "Chlorine Derivatives of Pyridine—Part V., Synthesis of $\alpha\alpha$ -Dichloropyridine and Constitution of Citrazinic Acid," by W. J. Sell, M.A., and F. W. Dootson, M.A. "Action of Fuming Nitric Acid on α -Dibromocamphor," by A. Lapworth, D.Sc., and E. M. Chapman.
"Electrolysis of Nitrogen Hydrides and of Hydroxylamine," by E. C. Szarvasy, Ph.D.
— Society of Arts, 4.30. "Our Work in India in the Nineteenth Century," by Sir William Lee-Warner, K.C.S.I., M.A. (This meeting will be held at the Imperial Institute).
— Royal Institution, 3. "The Senses of Primitive Man," by W. H. R. Rivers, M.A., M.D., &c.

FRIDAY, 19th.—Royal Institution, 9. "Flight," by The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

SATURDAY, 20th.—Royal Institution, 3. "Neglected Byways in Music" (with Musical Illustrations), by Sir Hubert H. Parry, Mus. Doc., M.A., D.C.L.

INSTRUCTION IN PURE CULTIVATION OF YEAST, According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts (brewers', distillers', wine, disease yeasts), moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufacturers, &c.

Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2095.

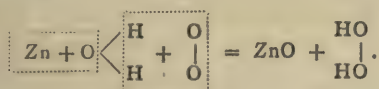
THE INFLUENCE OF WATER ON THE COMBUSTION OF CARBON MONOXIDE. A PLEA FOR "CONTACT ACTION."

By G. MARTIN.

BETWEEN the years 1882—1885 Traube showed in all cases of slow oxidation at ordinary temperature that—

1. In no case is there evidence that the atoms of the oxygen molecule are severed before oxidation proceeds (see Note A).
2. The atoms of the oxygen molecule are so firmly bound together that even substances like Na, K, S, C, &c., cannot sever the bonds between the oxygen atoms, and hence these substances remain unattached even when heated very intensely in dry oxygen gas.
3. Absolutely pure water carefully freed from air has no action on metals such as zinc, iron, lead, &c.
4. But the moment oxygen and water are allowed to act simultaneously on the metal, oxidation proceeds, and hydrogen peroxide (H_2O_2) is in all cases formed.

He therefore regards oxidation as due to a decomposition of the water molecule under the contrary attractions of the metal for the oxygen of the water molecule and the free oxygen gas present for the hydrogen of the water molecule, thus:—



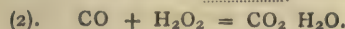
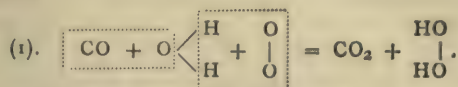
Notice that here the oxygen molecule does not break up, but combines with the hydrogen as a whole. It would hence appear that the conditions immediately preceding an oxidation at low temperature consist in a *complication*, not in a *simplification* or break down of the oxygen molecule as is usually believed.

In the above reaction, although the zinc tends by itself to decompose the water, yet the presence of a third body—oxygen—is necessary to determine the reaction. Indeed the oxygen here appears to act more by "contact" than anything else, and were it not that we can detect small quantities of H_2O_2 (which, however, are rapidly destroyed by side reactions), we should have a so-called "catalytic action" pure and simple. At higher temperatures, although the determining attractive power of the oxygen still remains, yet in consequence of the more violent motion of the atoms this attractive power is not sufficient to cause combination, but yet quite sufficient to ensure the progress of a chemical reaction.

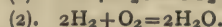
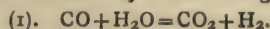
It appears that Prof. Dixon has no right to neglect the effect of this "contact action" of oxygen in determining the course of a reaction, especially as Traube's experiments show that oxygen possesses sufficient attractive power to form H_2O_2 . Although at higher temperature H_2O_2 may not be actually produced, yet the "tendency" for its production always remains, but is neutralised by the greater motion of the atoms (see Note B).

When Prof. Dixon, in 1884, discovered that dry carbon monoxide and oxygen gas will not explode, Traube, under the influence of his earlier experiments, put forward this theory to account for the action of water in rendering the

CO and O_2 mixture inflammable (compare previous equation):—



Prof. Dixon has, I believe, succeeded in proving that Traube made some erroneous statements, but he has not yet proved that Traube is wrong in principle. Prof. Dixon explains the reaction by the following equations:—



Now Prof. Dixon bases his first equation upon the fact that when CO and steam are heated together, reaction (1) partially takes place.

He contradicted Traube's assumptions by means of experiments on the explosion of mixtures of carbon monoxide and hydrogen containing insufficient oxygen for complete combustion.

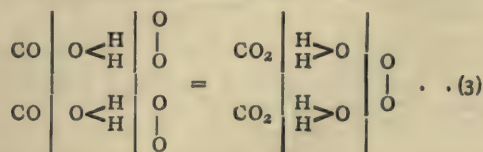
The case, then, is this:—Prof. Dixon states that because CO_2 and H_2 are formed when CO and H_2O are heated together; therefore when CO, H_2O , and O_2 are heated together, we also get hydrogen gas formed, which combines with free oxygen gas to form water, the oxygen having no independent effect in altering the character of the change.

I do not think Prof. Dixon is justified in assuming that experimental results deduced from one set of experiments under certain physical conditions—such, for instance, as a deficiency or absence of oxygen gas—apply to another set of experiments under totally different physical conditions—such as an excess or sufficiency of oxygen necessary for the complete combustion of the reacting materials, especially as Traube's experiments appear to indicate that oxygen exerts a certain "attractive force" on water which may totally change the course of a reaction.

The mere presence or absence of a substance may exert an enormous influence on the character or nature of the change.

A more probable view is that the explosion consists in a number of chemical reactions going on at one and the same time. As the relative masses of the reacting materials vary with the progress of the reaction, so too do the quantitative amounts of the several changes involved continually alter—one reaction predominating at one time, and another at another time, according to the varying amounts of the products of combustion present in the gas.

Thus at the beginning of the explosion, when there is an excess of steam and a sufficiency of oxygen, we probably get this reaction taking place (See Armstrong, "Presidential Address to Chem. Soc.," 1895).



When, however, the quantity of oxygen becomes more and more exhausted as the combustion proceeds, the reaction—



comes more and more into evidence.

I do not mean to imply that these are the only reactions taking place. There would probably be intermediate reactions between (3) and (4).

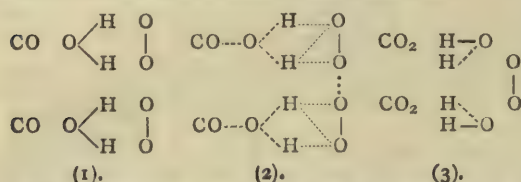
Now since we should expect (3) to proceed with less expenditure of energy than (4)—since in (3) the reaction

partakes of the nature of successive "link motion" between the molecules (see *Note C*), while in (4) we have an absolute disruption of the H_2O molecule, we should hence expect (3) to take place in the largest quantity, because it would proceed the most readily, but as the oxygen gas gets burnt up (4) should come more and more into evidence. (4) would probably proceed at a slower rate than (3), owing to the greater expenditure of energy necessary to bring it about.

If this view is correct a cinematographic series of photographs of the explosion should reveal a bright head of flame, followed by a tailing off of lesser intensity, or even waves, due to the different rates of propagation of the different reactions.

The tailing off should become more marked as the quantities of steam or oxygen present in the mixture diminish.

In (3) we can suppose with Traube that H_2O_2 first tends to be formed (see *Note D*), but that a more staple arrangement of the atoms immediately takes place thus:—



Shows the molecules before they are in close proximity to each other.

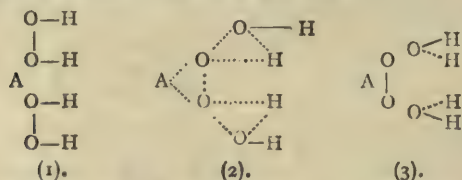
The dotted lines show the new distribution of strain among the atoms when in close proximity to each other. The above does not represent a chemical compound, it represents a "condition."

Shows how the decomposition proceeds under "contact" influence of the oxygen. It is the attraction of the oxygen both for the H and for itself that causes the decomposition to take place.

The change from (2) to (3) would be practically instantaneous, because it takes place *before* any H_2O_2 is actually produced. There is a mere tendency for the H_2O_2 to exist.

That such a mere tendency would have most important effects in determining chemical change cannot be doubted.

Contact action can thus be readily explained if we bear in mind the fact that molecules and atoms are in a state of violent motion. Thus we might have—



Old distribution of strain.

New distribution of strain.

Decomposition under new strain.

The attraction of any substance A for the oxygen of the hydroxyl molecules being insufficient to cause union, but quite sufficient to cause a new distribution of strain among the atoms of the molecules.

Thus, as the centre of force shifted, the relative dependency of the atoms on each other would alter, and, considering that the atoms are in a state of violent motion, it is very easy to conceive the momentous importance such a momentary re-distribution of strain among the atoms would have in determining the course of chemical change.

Dixon's hypothesis has yet another fault. It is not general enough. Although at the time it was advanced it was capable of explaining the particular effect produced by water in determining chemical action in the one particular case of CO and O, yet later work has shown us that this particular case stands not alone, but is one only of an

enormous number of cases where such an explanation as Dixon put forward is inadmissible, and a common solution must be extended to all.

How, for instance, can Prof. Dixon explain the fact that ammonium chloride does not dissociate in the absence of water, but sublimes unchanged?

On the "influence" theory here advanced it is readily explainable; the "pull" of the H_2O molecule on the already over-strained NH_4Cl molecule being sufficient to cause its disruption.

We are here reminded of the well-known phenomenon of "super-cooling." In this case we must suppose that when the substance is cooling below its solidifying point the presence of some foreign material by its "attractive" power alters the distribution of strain among neighbouring molecules, and hence alters the state of motion of their atoms and in consequence the substance quickly solidifies or changes its physical state.

In the case of NH_4Cl might not the H_2O molecule act mechanically like the foreign particles in the case of a supercooled liquid, and thus destroy the equilibrium of the over-strained NH_4Cl molecules? Once an ammonium chloride molecule has decomposed into NH_3 and HCl , the NH_3 and HCl act themselves like foreign particles and further the change, because part of their total energy is available for an external attraction.

The stability of the NH_4Cl molecule in this over-strained and abnormal condition might be explained as the stability of a system in motion—the momentum, so to speak, of the atoms in the molecule giving a certain amount of stability to the system. The presence of an external attraction (like that of a neighbouring H_2O molecule) might suffice to throw the atoms out of the grooves in which they run (speaking figuratively within the molecule, and hence cause a decomposition (see *Note D*), especially as the vapour is on the verge of decomposition. In the absence of such an external attraction there would be no reason why the state of motion within the molecule should not continue in virtue of its own inertia, and thus produce such phenomena as "super cooling", &c.

The reason why NH_4Cl molecules do not act like foreign particles towards each other, and thus mutually cause dissociation to take place, might be sought in the fact that the molecule has all its energy strained to the utmost in keeping together the tugging atoms, and hence has no energy left with which it can exercise an external attraction.

That water has an abnormal power of dissociating bodies in solution is well known, and is an argument for the above view.

NOTES.

A.—Traube cited the following in proof of the fact that no "nascent oxygen" atoms are present during a "slow" oxidation:—(1) If "nascent oxygen" were produced by shaking up zinc with atmospheric oxygen and water (in which case H_2O_2 is produced), an easily oxidisable substance such as indigo sulphonic acid would quickly be oxidised and decolourised; but this is found not to be the case, although H_2O_2 is formed (abstracts *Chem. Soc.*, 1882, p. 795). (2) Zinc, when shaken up with air and NH_3 , forms H_2O_2 ; but were the hypothetical active oxygen present, the NH_3 in the solution should be oxidised to NH_4NO_2 and NH_4NO_3 . No traces of these substances could be detected. (3) When KNO_3 is reduced by zinc, no active oxygen atoms are produced, for the reduction of KNO_3 proceeds as readily in the presence as in the absence of air. The NH_3 produced in the reduction is not oxidised to ammonium nitrite or nitrate, even when there is a large excess of air present, and this although H_2O_2 can be detected. (4) When acidulated water is electrolysed, the platinum electrodes being separated by a cylinder of some porous material, Traube finds that no H_2O_2 is produced at the + pole (where nascent oxygen is liberated) but only at the - pole

where the oxygen gas dissolved in the water can come into contact with the nascent hydrogen as it is evolved. Now if the nascent oxygen combined with the water to form H_2O_2 , we should certainly expect to find the H_2O_2 at the + pole, where the nascent oxygen is given off. Instead of this the H_2O_2 is only formed at the - pole, where the hydrogen is given off and can combine with the oxygen in the water about the - pole. In none of the above cases (and many others) could Traube detect the presence of active oxygen atoms, although at the same time oxidation of the water proceeded and also H_2O_2 was formed. It would appear then that a slow oxidation proceeds not by a breakdown of the oxygen molecule into atoms, but rather by a complicated double reaction.

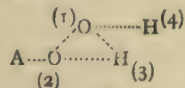
B.—At present a chemical attraction is only recognised when it is of sufficient strength to cause a chemical combination of the elements concerned. It cannot be doubted that many "chemical attractions" exist, but which are not evident because the attractive force is too feeble to cause an actual combination; nevertheless such a force might have important effects in determining the character of a reaction, although, indeed, no compound may actually be produced. This probably explains the so-called "catalytic" actions. Another point to be observed is that if a body exerts an attraction on another at some one temperature, it probably will still exercise an attraction at any other temperature—although the velocities of the atoms may so change that this constant attractive power will not exercise much control over the motion of the atoms—it is the motion that changes, not the attractive power.

C.—The energy absorbed by a "snapping" of one "bond" being immediately equalled or exceeded by the energy given out by the combination. If we imagine the molecules stretched in a chain, the attractions being equal on all sides of the constituent atoms, it is easy to see how an oscillatory movement of the atoms will propagate a chemical reaction with very little expenditure of energy.

D.—It may be conceived that a chemical reaction takes place in many cases by a preliminary association of the molecules together. This "association" need not necessarily represent an instantaneous "compound," it merely represents a "condition." During this period of association the relative "strains" among the atoms must shift, and thus prepare for a break up of the molecules, and as a result of the violent internal movements of the atoms in the molecules this "shifting of the strains" immediately intensifies the strain on some groups of atoms and weakens it in others, and hence we get groups of atoms detaching themselves to form new chemical compounds. Traube's work favours this view. (See also Dr. Armstrong's Presidential Address to the Chemical Society in 1895, where strong arguments are put forward for a preliminary "association" of molecules immediately preceding a chemical reaction). Now "contact action" is simply a case of this "association" of molecules, but in this case, although the force is sufficient to cause decomposition, yet it is not sufficient to cause combination as in the action of finely divided gold on the H_2O_2 , &c., &c. To understand what is meant by the word "strain" among the atoms, the reader is referred to Mendeleeff's "Principles of Chemistry," vol. ii., Appendix i. (1897), where it is pointed out that we have strong reason (from spectroscopic and other physical and chemical work) to believe that the atoms of a molecule are in motion, and in consequence of this motion they exert a "pull" on each other. Now, by Newton's "Third Law of Motion," that "Action and Reaction are equal"; if an atom A exerts a force on an atom B, then B exerts an equal force on A. Contact action acquires a new significance if looked upon in the light of this conception. Consider, for example, the molecule—



whose atoms are numbered 1, 2, 3, and 4. According to the above the pull of each H atom on the neighbouring O atom is equal and opposite to the pull of the O atom on the H atom, and in turn the pulls of the O atoms on each other are equal, so that a state of dynamical equilibrium reigns throughout the molecule.



If now a substance A be brought up close to one of the O atoms (2), then owing to the presence of A the position of 2 will be altered in respect to 1, 3, and 4, and we should now expect that these atoms, 1, 3, and 4, would now shift their positions so as to exercise a joint pull on 2 equal and opposite to the pull exerted on them by atom 2, *part of the pull formerly expended on them by 2 now being transferred to A*. Now as these atoms shift their relative positions so as to automatically adjust themselves to the new state of equilibrium, it is easily understood if we bear in mind the internal motions of the atoms, how such a shifting might result in a decomposition of the molecule.

Merchant Venturers' Technical College,
Bristol.

THE ESTIMATION OF AMMONIA, NITRIC ACID, AND NITROUS ACID IN NATURAL WATERS.

By L. N. WINKLER.

THE estimation of the ammonia in natural waters is generally done by the colorimetric method, with the aid of Nessler's solution. The method followed consists in removing the calcic and magnesian salts from the water under examination, and adding to the clear liquid a certain quantity of Nessler's solution. In the presence of ammonia the mixture takes a yellowish tinge. A solution of chloride of ammonium of known strength is then added to exactly the same quantity of distilled water, free from ammonia, until the tint coincides exactly with that obtained with the natural water. When the Nessler's solution is dropped in to the distilled water, and the chloride of ammonium then added drop by drop, the former becomes cloudy, and can no longer be examined colorimetrically. Again, the typical solutions must be freshly prepared for each series of experiments, by mixing large quantities of water with small quantities of chloride of ammonium. I have found that by adding, besides the Nessler's solution, a solution of Seignette salt, or any other tartrate, the chloride of ammonium can be added without any precipitate being formed. The use of the Seignette salt is so advantageous that the elimination of the calcium and magnesium is superfluous; now it is exactly this factor which makes the colorimetric examination in question so long and difficult. We can, however, make a sufficiently exact estimation of the ammonia present in natural waters by adopting the following method. Two flasks are required, fitted with ground glass stoppers, and of a little more than 100 c.c. capacity; into one of these flasks we pour 100 c.c. of the water to be examined, and into the other 100 c.c. of distilled water free from ammonia; to each of these flasks are then added 2 or 3 c.c. of a solution of Seignette salt, saturated at the ordinary temperature, and a similar quantity of Nessler's solution. To the flask containing the distilled water we then add, drop by drop from a graduated burette, a solution of chloride of ammonium, of which each c.c.

contains a quantity of chloride equal to 0.1 m.grm. of ammonia. The flask is frequently shaken, and the addition of the chloride stopped when the distilled water has taken the same tint as the water under examination. The volume of the chloride of ammonium used enables us to calculate the amount of ammonia contained in 1 litre of the water. The solution of chloride of ammonium is prepared by dissolving 0.315 grm. of the salt in 1 litre of water; the best form of burette to use is one of Gay-Lussac's, of about 10 c.c. capacity, with an internal diameter of 6 or 8 m.m. The method described does not require the use of a colorimeter, and gives very exact results. The following are a few examples:—

Ammonia added to 1 litre.	Ammonia found in 1 litre.	Ammonia added to 1 litre.	Ammonia found in 1 litre.
M.grm.	M.grm.	M.grm.	M.grm.
0.48	0.46	0.47	0.49
1.50	1.55	1.22	1.16
5.00	4.72	1.85	1.98

When the water to be examined is cloudy it must be filtered, using only a small filter, and rejecting the first 100 or 200 c.c.

The quantitative estimation of the nitric acid in natural waters is most easily effected by means of the brucine reaction (G. Lunge and A. Lucoff, *Zeitschr. für Angew. Chem.*, 1894, No. 12).

When we mix one volume of a very dilute solution of a nitrate (1:100,000) with two volumes of concentrated sulphuric acid, and dissolve in this liquid, when cold, a small quantity of brucine, a beautiful rose-red colouration is produced. After standing for a considerable time the colour changes to an orange-yellow, and finally takes a citron-yellow tint; but on adding the brucine to the warm solution, the red colour produced remains for an instant only, and immediately gives place to the yellow tint. The intensity of the colour is in direct relation to the quantity of nitric acid present.

These facts enable us to estimate the quantity of nitric acid present in natural waters in a few minutes; the following is the method of procedure:—Two small flasks of 50 c.c. are used; into one of these we pour 10 c.c. of the water to be examined, and into the other 10 c.c. of distilled water. To each of these flasks is added 1 c.c. of a 2 per cent solution of sulphate of brucine, and then 20 c.c. of concentrated sulphuric acid. The nitrated water becomes yellow, while the distilled water remains colourless, that is, if the sulphuric acid is free from nitrates. We then add, drop by drop, to this latter solution, while still warm, a solution of potassic nitrate, of which each c.c. contains 0.1 m.grm. of nitric acid. After the addition of each drop the flask must be shaken, and the colour compared with that of the other one; when the tints agree the estimation is complete. The number of c.c. used, multiplied by 100, gives the quantity of nitric acid contained in 1 litre of the water under examination. When the water contains only traces of nitric acid, and very exact results are required, 50 c.c. of the water should be taken, and 100 c.c. of sulphuric acid.

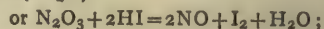
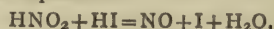
The solution of potassic nitrate contains 0.187 grm. of the pure dry salt per litre; thus, each c.c. is equivalent to 0.1 m.grm. of anhydrous nitric acid, N_2O_5 . The accuracy of the results obtained by this method is fairly good, as can be seen from the following figures:—

Nitric acid added to 1 litre.	Nitric acid found in 1 litre.	
	With 10 c.c. of water.	With 30 c.c. of water.
M.grms.	M.grms.	M.grms.
7.0	6.3	
2.0	2.5	2.0
13.0	11.8	13.0
0.5	0.9	0.7
21.0	21.7	
31.0	29.7	

It may reasonably be asked whether the organic

matter contained in natural waters does not have an unfavourable influence on the results obtained. My experiments show that such is not the case. By this method I have estimated the nitric acid in a highly contaminated water, then in another portion of the same water I dissolved a small quantity of permanganate of potash, added a few drops of concentrated sulphuric acid, and heated on the water-bath for about half-an-hour. After having destroyed the excess of permanganate by means of oxalic acid, I estimated the nitric acid, and did not find any variation from the results first obtained. This is sufficient proof that the estimation of the nitric acid can be effected even in the presence of fairly large quantities of organic matter. When the water contains ferrous salts, they must be oxidised to the ferric state by means of permanganate. As nitrous acid acts on brucine in the same manner as nitric acid, it must be first oxidised to the state of nitric acid by permanganate, and deducted from the nitric acid found.

To detect nitrous acid in natural waters a small quantity of potassic iodide must be dissolved, then a little starch solution added, and a few drops of sulphuric acid. In the presence of nitrous acid, the iodide is set free and colours the starch blue. The reaction takes place according to the equation—



one molecule of N_2O_3 thus sets at liberty two atoms of iodine, so that, by titrating the iodine liberated with a solution of hyposulphite of soda, we can calculate the quantity of nitrous acid present. The titration of the iodine, however, has not a very definite termination, even if we use a larger amount of hyposulphite of soda than is theoretically required; the solution, which is decolourised with great difficulty, immediately returns to its original colour. This phenomenon is due to the presence of binoxide of nitrogen, which, as in the manufacture of sulphuric acid, here plays the important part of absorbing oxygen.

The protoxide of nitrogen combines with the dissolved oxygen, to form the binoxide, which sets iodine and hydriodic acid free, and is itself reduced to the state of protioxide. But the question bears a different complexion when the oxygen which interferes with the reaction is driven off. If we acidulate the water, and then add a carbonate or bicarbonate, the carbonic acid formed drives off not only the oxygen entangled in the water, but also the dissolved oxygen. On then dissolving iodide of potassium in the sample, it is perfectly easy to titrate the iodine set free without fearing the interference of the unfavourable factors which were just referred to. The estimation of nitrous acid may thus be effected in the following manner:—Take 100 c.c. of the water under examination; if it is cloudy or coloured yellow by ferric hydrate, it must be cleared by sedimentation and filtration. The sample taken is placed in a flask of 200 c.c. capacity with a long narrow neck, 20 c.c. of 10 per cent hydrochloric acid and 2 or 3 c.c. of starch solution are added. To this mixture is then gradually added 5 grms. of pure crystals of potassic bicarbonate, about 1 grm. at a time, waiting a little while after each addition, so that the froth does not run over. When the greater part of the salt (four-fifths) has been added, a small crystal of potassic iodide is thrown in, and then the remainder of the bicarbonate, so that the binoxide of nitrogen which is formed by the action of the nitrous acid on the hydriodic acid is driven out of the flask. The iodine set at liberty is titrated with a dilute solution of hyposulphite of soda, of which each c.c. contains 0.1 m.grm. of N_2O_3 , a solution which can be prepared by diluting 26.3 c.c. of a decinormal solution to 1 litre. After titration the liquid should remain colourless for ten minutes; if it does not, it shows that the oxygen or the binoxide of nitrogen has been incompletely expelled.

The following figures show the great accuracy with

which even very small quantities of nitrous acid can be estimated:—0.406 grm. of nitrate of silver was dissolved in warm water, and an equal quantity of sodic chloride was added; on cooling, the cloudy liquid was made up to 1 litre and allowed to stand; the supernatant portion then constituted a solution of sodic nitrate containing 0.1 m.grm. of nitrous acid (N_2O_3) per c.c. The results obtained with different volumes of this solution are given below:—

N_2O_3 taken per litre.	N_2O_3 found per litre.	N_2O_3 taken per litre.	N_2O_3 found per litre.
1.00 m.grm.	0.96 m.grm.	1.00 m.grm.	0.95 m.grm.
3.00 "	3.00 "	3.00 "	3.00 "
5.00 "	4.95 "	5.00 "	5.11 "

It seemed of interest to make a few experiments with a view to finding out whether it is possible to estimate nitrous acid in the presence of nitric acid and ammonia. These two bodies were estimated by the method previously described; the results are given below.

Nitrous acid.		Ammonia.		Nitric acid.	
Taken per litre.	Found per litre.	Taken per litre.	Found per litre.	Taken per litre.	Found per litre.
M.grm.	M.grm.	M.grm.	M.grm.	M.grm.	M.grm.
0.4	0.34	0.4	0.42	3.0	2.9
1.4	1.32	2.4	2.00	5.0	5.2
3.0	3.03	4.0	3.59	14.0	13.5

I am therefore of the opinion that these results are most favourable to the method described, but I must once more repeat that the complete expulsion of the air is an essential condition to be observed—a condition that will be fully realised by following the directions given. I should also add that ferric salts also set iodine at liberty from a solution of hydriodic acid, but they can easily be removed by adding a solution of sodic hydrate, free from nitrite, to the water, and filtering. However, in natural waters the iron is nearly always found in the state of ferrous bicarbonate, and the ferrous salts have no action on iodides.—*Chemiker Zeitung*, 1899, No. 43, p. 454.

WORKS LABORATORY BURETTE RACK.

By C. SORDES ELLIS, A.I.C., F.C.S.

THE instability of the ordinary burette stand is, I think, a fact well known to all chemical students. When college is left, and the chemist finds himself in a works laboratory, the bugbear of shaking burettes is still with him, and in an accentuated form.

To eliminate this inconvenience, and to greatly facilitate work, I have designed and had erected a rack, the end of which is shown in the accompanying diagram. Fig. 1 shows front view of a portion. W X and Y Z are two strips of wood, 1 inch by 2 inch and 5 feet long, with narrow edges to the front, held together at a distance apart of 18 inches by three pieces of wood (one only is shown, S S) morticed into the long pieces. The dotted lines A A A are two shelves firmly fixed to the wall. To the shelves six strips of wood are screwed and morticed into the uprights (two are shown at s and s). The whole is made of pitch-pine, and fixed plumb at any convenient distance from the shelves behind and the bench beneath. In a second rack I had put up, I found that one support from top to middle upright, and two from bottom shelf to end ones, were quite sufficient to hold the whole firmly to the shelves. At convenient distances apart semi-circular depressions, G, are cut on the front of the frame, both top and bottom, in a perpendicular line.

In Fig. 2 will be seen details of the clip. It is made of 1/16 inch brass, and 1/2 inch or 5/8 inch wide. A square, K, is hinged at B to a longer piece, with a slight depression at G' and a slit at D. On the other side of G is another

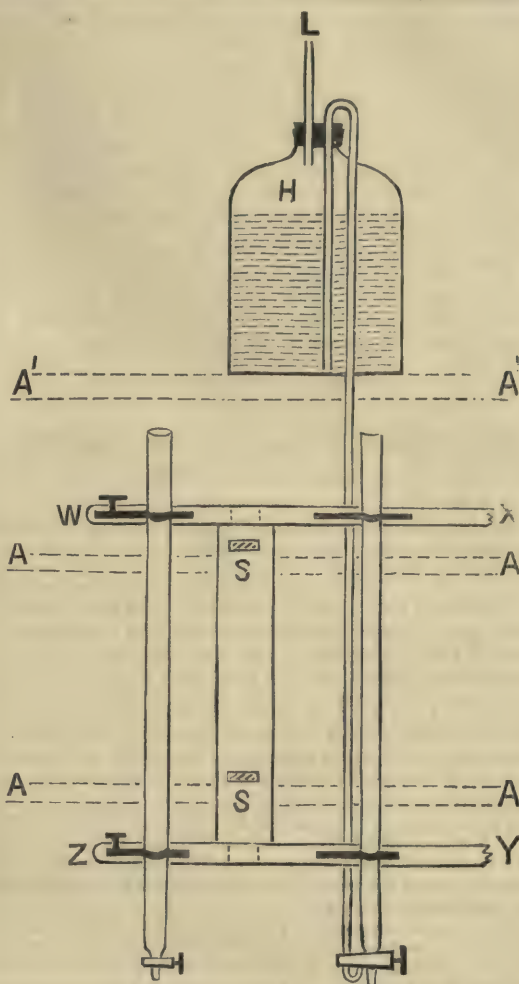


FIG. 1.

WORKS LABORATORY BURETTE RACK

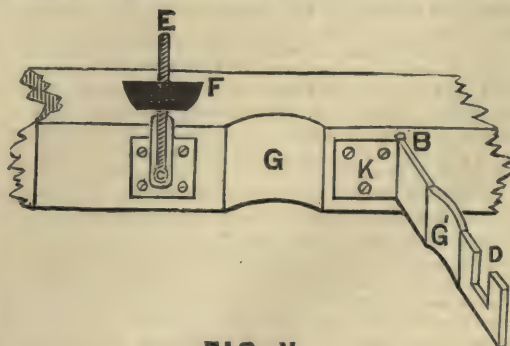


FIG. II.
DETAILS OF CLIP & ATTACHMENT

square of brass, with a slotted projection brazed on the back. A piece of brass rod, E, is hinged at C so as to move forward; E has a thread cut on it which fits a

milled edge nut, F; G and G' are both lined with thick baize or swansdown cloth. The whole is so arranged that when closed E will fall into the slit D, and on screwing up F the movable part will be brought up tight. The spring of the brass holds the burette firmly in position, perfectly rigid and perpendicular, being held by clips at top and bottom. If the rack is made to the dimensions given above, it will be found to take six burettes comfortably.

I have found the arrangement shown in the second burette, Fig. 1, most handy when large quantities of a standard solution are in constant use. The bottle, H, on a shelf, A' A', is fitted with a cork, through which two holes have been bored; into one a short piece of glass tubing is inserted, and the end drawn out to a very fine point; through the other hole a long syphon tube is placed, which is joined up to the burette having a two-way tap.

ON THE VOLUMETRIC ESTIMATION OF CERIUM.*

By PHILIP E. BROWNING.

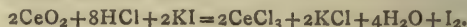
SOME forty years ago Bunsen (*Annalen d. Chem. u. Phar.*, cv., 49) showed that the oxide obtained by the ignition of cerium oxalate might be estimated volumetrically by bringing it in contact with potassium iodide and strong hydrochloric acid, and determining the iodine set free. This method may be briefly described by a translation of part of the original article:—"The substance to be determined is weighed out in a glass flask of from 10 to 15 c.c. capacity, a few crystals of potassium iodide are added, and the neck of the flask is drawn out by the aid of a blowpipe to a narrow opening. The flask is filled almost to the narrowing of the neck with hydrochloric acid which is free from chlorine or iron chloride, and a little sodium carbonate is added in order to displace the last trace of air by carbon dioxide. The flask is then closed by sealing off the neck in the blowpipe, and warmed in a water-bath until the cerium compound is completely dissolved, and the quantity of iodine set free is determined by iodometric analysis."

The anhydrous dioxide prepared by the ignition of the oxalate or hydroxide is very slowly acted on by acids, especially when pure (Rose, *Handbuch der Analytischen Chemie*, Band. i., 219). For this reason the method which Bunsen described has remained the only one adapted to the satisfactory volumetric estimation of the ignited dioxide.

Two portions of the dioxide were prepared by treating the crude cerium chloride in concentrated solution with gaseous hydrochloric acid (Dennis and Magee, *Zeitschr. f. Anorgan. Chem.*, iii., 260) to saturation to remove the iron. The cerium chloride was then dissolved in water, potassium hydroxide added in excess, and chlorine gas passed until the precipitate became distinctly orange in colour and the solution gave a strong odour of chlorine (Mosander, *Phil. Mag.*, xxviii., 241; Dennis, *Zeit. f. Anorgan. Chem.*, vii., 252). This operation was repeated until a portion of the precipitate dissolved in acid showed no didymium absorption bands when examined before the spectroscop. The whole precipitate of the dioxide was then dissolved in hydrochloric acid, and the oxalate precipitated by ammonium oxalate in large excess. The precipitated oxalate was then washed thoroughly with hot water until the washings gave no test for hydrochloric or oxalic acids and ignited to the dioxide. Another portion of the dioxide was later prepared by precipitating a solution of pure cerium chloride by means of ammonium oxalate, washing and igniting as described. The dioxide in all three cases was of a light chamomile colour, and uniform results were obtained from the three portions.

A Modification of the Method of Bunsen (with G. A. HANFORD and F. J. HALL).

Weighed portions of the pure cerium dioxide were placed in small glass stoppered bottles of about 100 c.m.³ capacity, together with a gm. of potassium iodide free from iodate and a few drops of water to dissolve the iodide. A current of carbon dioxide was passed into the bottle for about five minutes to expel the air, 10 c.m.³ of pure strong hydrochloric acid were added, the stopper inserted, and the bottle heated gently upon a steam radiator for about one hour until the dioxide dissolved completely and the iodine was set free. After cooling the bottle, to prevent loss of iodine upon removing the stopper, the contents were carefully washed into about 400 c.m.³ of water, and titrated with standard sodium thiosulphate to determine the amount of iodine liberated according to the well-known reaction—



A few blank determinations were carried through in the bottles without the presence of the cerium dioxide to determine the amount of iodine set free under these conditions. The amount obtained was uniformly equal to 0.04 c.m.³ of the 1/10 N iodine solution which was taken as the correction and applied to all the determinations. The results follow in Table I.

TABLE I.

	CeO ₂ taken. Grm.	CeO ₂ found. Grm.	Error. Grm.
1.	0.1000	0.0994	0.0006—
2.	0.1032	0.1034	0.0002+
3.	0.1016	0.1017	0.0001+
4.	0.1054	0.1041	0.0013—
5.	0.2010	0.2021	0.0011+
6.	0.1104	0.1109	0.0005+
7.	0.1914	0.1907	0.0007—
8.	0.1604	0.1603	0.0001—
9.	0.2146	0.2145	0.0001—
10.	0.1108	0.1099	0.0009—
11.	0.1346	0.1347	0.0001+
12.	0.1540	0.1534	0.0006—
13.	0.1976	0.1968	0.0008—
14.	0.1230	0.1240	0.0010+
15.	0.1199	0.1201	0.0002+
16.	0.1524	0.1528	0.0004+
17.	0.1212	0.1211	0.0001—
18.	0.1528	0.1543	0.0015+

In order to obtain a further check upon the accuracy of the method, portions of the cerium dioxide were weighed out and placed in a distillation apparatus previously employed for similar purposes and described in former articles from this laboratory, viz., a Voigt flask, serving as a retort, sealed to the inlet tube of a Drexel wash-bottle, used as a receiver, the outlet tube of which was trapped by sealing on Will and Varrentrapp absorption bulbs. In the retort the cerium dioxide together with 15 c.m.³ of water, 1 gm. of potassium iodide, and 10 c.m.³ of pure strong hydrochloric acid, were placed. In the receiver were 100 c.m.³ of water and 2 to 3 grms. of potassium iodide, and in the bulbs a dilute solution of potassium iodide. Before adding the hydrochloric acid a current of carbon dioxide was passed through the apparatus for some minutes. After adding the acid, the liquid was boiled in the current of carbon dioxide* to a volume of 15 c.m.³, when the free iodine had almost completely left the retort and passed into the receiver, and the apparatus was allowed to cool.

The iodine in the receiver was titrated directly with sodium thiosulphate, and that in the retort after dilution of the residue to about 400 c.m.³, the later amount seldom exceeding the equivalent of a few drops of 1/10 N iodine solution.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1899, vol. viii., No. 48.

* The carbon dioxide gas was furnished by a Kipp generator from marble and hydrochloric acid of one-half strength, both of which had been boiled previously to remove all air.

The results follow in Table II.

Here also blank determinations were made, but no correction was found to be necessary.

An attempt early in the work to titrate by an alkaline arsenite the iodine liberated, after neutralising the hydrochloric acid, brought out some curious results which seem worthy of mention.

TABLE II.

	CeO ₂ taken. Grm.	CeO ₂ found. Grm.	Error. Grm.
1.	0.1028	0.1013	0.0015—
2.	0.2060	0.2055	0.0005—
3.	0.2014	0.2012	0.0002—
4.	0.1716	0.1711	0.0005—
5.	0.0974	0.0972	0.0002—
6.	0.1600	0.1587	0.0013—
7.	0.1268	0.1254	0.0014—
8.	0.1276	0.1268	0.0008—
9.	0.1620	0.1612	0.0008—
10.	0.1016	0.1011	0.0005—
11.	0.1548	0.1543	0.0005—
12.	0.1352	0.1342	0.0010—

In these experiments the contents of the bottles after the cerium had dissolved were carefully washed into a Drexel wash-bottle, upon the inlet tube of which was fused a thistle tube with a stopcock, and to the outlet tube a Will and Varrentrapp absorption trap. In the trap a solution of potassium iodide was placed, and through the thistle tube a saturated solution of potassium bicarbonate was added to complete neutralisation of the acid. Any iodine carried mechanically by the carbon dioxide should be held by the potassium iodide solution in the trap. After neutralisation the free iodine was titrated by standard arsenious oxide solution. The results appear in Table III.

TABLE III.

	CeO ₂ taken. Grm.	CeO ₂ found. Grm.	Error. Grm.
1.	0.1000	0.0987	0.0013—
2.	0.1005	0.0981	0.0024—
3.	0.1030	0.1009	0.0021—
4.	0.1500	0.1475	0.0025—
5.	0.1030	0.1005	0.0025—
6.	0.1010	0.0988	0.0022—
7.	0.1510	0.1508	0.0002—
8.	0.1530	0.1485	0.0045—
9.	0.2045	0.2011	0.0034—
10.	0.2000	0.1958	0.0042—
11.	0.1334	0.1302	0.0032—
12.	0.1354	0.1330	0.0024—
13.	0.1312	0.1294	0.0018—
14.	0.1308	0.1277	0.0031—
15.	0.1060	0.1042	0.0018—
16.	0.1602	0.1567	0.0035—
17.	0.1504	0.1488	0.0016—

As will be seen by the table, an average error of about 2 per cent runs through the entire set. The natural conclusion would be that the cerium dioxide contained some impurity; but, as the first, second, and third samples, very carefully prepared, gave the same results, it seemed necessary to look elsewhere for an explanation. Two possible causes suggested themselves: first, mechanical loss during the process of neutralisation, and second, the possible formation, under the conditions, of iodine chloride, which if formed would in the process of neutralisation probably take the form of potassium chloride, iodide, and iodate, and thus some of the originally free iodine would be withdrawn from the amount titrated. To test these theories, portions of the 1/10 N iodine solution roughly equivalent to the amounts of iodine set free by 0.1 and 0.2 gm. of CeO₂ were drawn off into bottles previously filled with carbon dioxide, treated with the usual amount of strong hydrochloric acid (10 c.m.), and, after standing from

thirty to forty-five minutes, neutralised and titrated as already described. The results were most interesting, and seemed to show a loss of iodine closely equivalent to that shown by the results of Table III., and proportional to the amount of iodine originally present. A few determinations were carried through in the same way, except that the neutralisation was omitted and dilution and titration with thiosulphate substituted. These showed a loss of iodine well within the limits of such a process. The results follow in Table IV.

TABLE IV.

With Arsenious Oxide.

	Iodine 1/10 N taken. C.m.s.	Iodine 1/10 found. C.m.s.	Error. C.m.s.	Equivalent error on CeO ₂ . Grm.
1.	5.22	5.07	0.15—	0.0026—
2.	5.09	4.97	0.12—	0.0021—
3.	5.10	4.97	0.13—	0.0022—
4.	5.66	5.47	0.19—	0.0033—
5.	5.10	4.97	0.13—	0.0022—
6.	10.22	9.97	0.25—	0.0043—
7.	10.21	9.97	0.24—	0.0041—

With Sodium Thiosulphate.

	Iodine 1/10 N taken. C.m.s.	Iodine 1/10 found. C.m.s.	Error. C.m.s.	Equivalent error on CeO ₂ . Grm.
1.	5	5.01	0.01+	0.0002+
2.	5	4.99	0.01—	0.0002—
3.	10	10.02	0.02+	0.0003+
4.	10.08	10.12	0.04+	0.0007+

(To be continued).

THE
IODOMETRIC DETERMINATION OF GOLD.*

By F. A. GOOCH and FREDERICK H. MORLEY.

In a recent attempt to measure small amounts of gold in solution by titrating with sodium thiosulphate the iodine set free in the action of an excess of potassium iodide upon auric chloride, Peterson (*Zeit. fur Anorg. Chem.*, xix., 63) has been led to conclude that, on the average, one-half more thiosulphate is used up in changing the characteristic starch iodide blue to the faint rose colour which precedes entire bleaching than is called for upon the theory that the thiosulphate is simply converted to the tetrathionate in the usual manner. Peterson explains the anomaly upon the hypothesis that, besides acting upon the free iodine, the thiosulphate is used up coincidentally by interaction with the aurous salt, formed in the reduction, with formation of a gold sodium thiosulphate on the type of the well-known silver sodium thiosulphate. The reaction of this hypothesis is in the nature of things most improbable, since there is no reason to suppose that the soluble double thiosulphate could resist the action of the free iodine which is present to the end—the appearance of the rose colour,—and our study of the reaction of sodium thiosulphate upon the mixture of gold chloride and potassium iodide, the account of which follows, discloses no evidence of the consumption of more thiosulphate than is demanded by the usual theory, which postulates the simple formation of the tetrathionate by the interaction of the thiosulphate and free iodine.

It appeared in the course of our preliminary experimentation that, while practically similar results were obtained by adding the thiosulphate until the blue of the starch iodide had changed to rose, the indications were somewhat more concordant when the final rose colour was developed by adding iodine to the solution from which the blue had been bleached to colorlessness by a slight excess of the thiosulphate.

It appeared, also, that the reduction of the auric salt,

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, October, 1899.

with the consequent liberation of iodine, is conditioned by the volume of the solution, the mass of the iodine present, and the time of action.

The following statement, in which each result is the average of several titrations in close agreement, shows the effect upon the immediate evolution of iodine brought about by adding varying amounts of water to the gold solution before introducing the iodide, and the effect of different amounts of iodide at different dilutions.

Grm.	Potassium iodide.					Gold chloride. 0.00087	Volume before the addition of the thio-sulphate. C.m.
	0.01	0.02	0.05	0.1	0.2		
Sodium thiosulphate, nearly N/100. c.m.s.	0.81	0.81	0.81	0.82	0.84	"	15
	0.77	0.78	0.80	0.81	0.81	"	25
	0.74	0.72	0.78	0.79	0.80	"	50
	0.61	0.61	0.68	0.76	0.79	"	100
	0.45	0.49	0.60	0.72	0.75	"	200

It is evident that for the smaller amounts of iodide the liberation of iodine decreases rapidly with the dilution. The larger amounts at the highest concentration show readings a trifle above the normal—perhaps because the well-known effect of concentrated solutions of a soluble iodide upon the delicacy of the starch end-color begins to appear. At volumes lying between the limit of 25 c.m.³ and 50 c.m.³, 0.1 gm. of potassium iodide is an appropriate amount to use; at a volume of 15 c.m.³, 0.01 gm. to 0.05 gm. of the iodide will do the work; and at lower dilutions, as will appear in the tabular statements to follow, even less of the iodide is effective.

In the series of experiments of which the details are given in Table I., use was made of a solution of pure gold chloride containing 0.8710 gm. to the litre—as determined by careful precipitation in the usual manner by ferrous sulphate, and by an alkaline solution of formaldehyde, according to the method of Vanino (*Ber. D. Chem. Gesellsch.*, xxxi., 1763). A nearly centinormal solution of iodine was prepared by diluting to a litre 100 c.m.³ of nearly decinormal iodine in potassium iodide carefully standardised against exactly decinormal arsenious acid. A nearly centinormal solution of sodium thiosulphate (containing 1.7012 gm. of Na₂S₂O₃ to the litre) was made by diluting to a litre 100 c.m.³ of a nearly decinormal solution of that reagent which had been standardised carefully against the standard iodine prepared as described. The solution of potassium iodide employed contained 10 grms. of that salt in the litre.

In conducting the experiments, a convenient amount of the solution of gold chloride was drawn from a burette, potassium iodide was introduced in the amounts indicated (always several times the theoretical equivalent of the gold, and more than enough to dissolve the aurous iodide precipitated at first), a sufficiency of clear starch indicator was added, the starch blue was bleached by the thio-sulphate, and the iodine was added until the liquid assumed a faint rose colour. Upon the theory that potassium iodide sets free two atoms of iodine for every molecule of auric chloride (or every atom of gold) present, and that the thiosulphate acts only upon the free iodine to form the tetrathionate in the usual manner, every c.c. of the thiosulphate solution used in the reaction after deducting the amount equivalent to the iodine introduced to get the end-colour, should represent—

$$\frac{197.3}{2(158.22)} \times 0.0017012 = 0.001061 \text{ gm. of gold.}$$

Plainly, these results accord reasonably with the theory that two molecules of the thiosulphate are the equivalent in this reaction of two atoms of iodine and one atom of gold. There is no evidence whatever of the excessive action affirmed by Peterson.

The strength of the standard solutions used in the experiments described was such that an error of 0.01 c.m.³ in reading the volumes used would correspond to an error

TABLE I.

Gold chloride		= 0.8710 to 1 litre.					
Sodium thiosulphate, nearly N/100		= 1.7012 " "					
Iodine, nearly N/100		= 1.3697 " "					
(Volume at beginning of titration approximately 50 c.m. ³).							
	AuCl ₃ taken.	KI used.	Na ₂ S ₂ O ₃ found.	Theory for gold.	Error.	Per cent.	
	C.m.s.	Grm.	C.m.s.	Grm.	Grm.		
1.	5	0.05	4.02	0.00426	0.00435	-0.00009	2.1
2.	5	0.05	4.01	0.00425	0.00435	-0.00010	2.3
3.	5	0.05	4.06	0.00431	0.00435	-0.00004	0.9
4.	5	0.05	4.07	0.00432	0.00435	-0.00003	0.7
5.	5	0.05	4.04	0.00428	0.00435	-0.00007	1.6
6.	10	0.08	8.17	0.00867	0.00871	-0.00004	0.5
7.	10	0.08	8.15	0.00864	0.00871	-0.00007	0.8
8.	10	0.08	8.16	0.00865	0.00871	-0.00006	0.7
9.	10	0.08	8.15	0.00864	0.00871	-0.00007	0.8
10.	10	0.08	8.19	0.00869	0.00871	-0.00002	0.2
11.	10	0.08	8.46	0.00897	0.00871	+0.00026	3.0
12.	10	0.08	8.24	0.00874	0.00871	+0.00003	0.3

TABLE II.

A.

Gold chloride = 0.871 to 1 litre.
Sodium thiosulphate, nearly N/100 = 1.7012 " "
Iodine, nearly N/100 = 1.3697 " "
(Solution of gold chloride not diluted before mixing with potassium iodide).

	AuCl ₃ taken. C.m.s.	KI taken. Grm.	Na ₂ S ₂ O ₃ used. C.m.s.	Gold taken. Grm.	Gold found. Grm.	Error. Grm.
1.	10	0.01	0.83	0.00087	0.00088	+0.00001
2.	10	0.01	0.83	0.00087	0.00088	+0.00001
3.	10	0.01	0.80	0.00087	0.00085	-0.00002
4.	10	0.02	0.84	0.00087	0.00089	+0.00002
5.	10	0.02	0.88	0.00087	0.00093	+0.00006
6.	10	0.02	0.82	0.00087	0.00087	0.00000
7.	10	0.02	0.88	0.00087	0.00093	+0.00006
8.	10	0.02	0.83	0.00087	0.00088	+0.00001
9.	10	0.10	0.80	0.00087	0.00085	-0.00002
10.	10	0.10	0.82	0.00087	0.00087	0.00000
11.	10	0.01	0.83	0.00087	0.00088	+0.00001
12.	9	0.01	0.73	0.00078	0.00077	-0.00001
13.	8	0.01	0.65	0.00070	0.00069	-0.00001
14.	7	0.01	0.58	0.00061	0.00061	0.00000
15.	6	0.008	0.51	0.00052	0.00054	+0.00002
16.	5	0.008	0.41	0.00043	0.00044	+0.00001
17.	4	0.005	0.35	0.00035	0.00037	+0.00002
18.	3	0.005	0.24	0.00026	0.00026	0.00000
19.	2	0.003	0.21	0.00017	0.00022	+0.00005
20.	1	0.003	0.10	0.00009	0.00011	+0.00002

B.

Gold chloride = 0.871 to 1 litre.
Sodium thiosulphate, nearly N/1000 = 0.17012 " "
Iodine, nearly N/1000 = 0.13697 " "

21.	10	0.01	8.39	0.000871	0.000890	+0.000019
22.	9	0.01	7.45	0.000784	0.000790	+0.000006
23.	8	0.01	6.30	0.000697	0.000668	-0.000029
24.	7	0.008	5.50	0.000610	0.000583	-0.000027
25.	6	0.008	5.12	0.000523	0.000543	+0.000020
26.	5	0.005	4.23	0.000435	0.000449	+0.000014
27.	4	0.005	3.38	0.000348	0.000358	+0.000010
28.	3	0.003	2.55	0.000261	0.000270	+0.000009
29.	2	0.003	1.71	0.000174	0.000181	+0.000007
30.	1	0.003	0.90	0.000087	0.000095	+0.000008

of 0.00001 gm. of gold. It is not to be expected that such readings can be trusted ordinarily to a higher degree of accuracy than 0.02 c.m.³. In case all three solutions

should be read to this limit of accuracy with the errors of all lying in the same direction, the summation of errors would correspond to 0.00006 grm. of gold.

In the experiments in Table II., therefore, solutions obtained by properly diluting those of the previous series were employed. The use of a more dilute solution of gold obviated the necessity for diluting the mixture of gold chloride and the iodide before titrating with the thio-sulphate. It was found, however, that when the N/1000 solution of iodine is employed a correction of 0.1 c.m.³ for volumes not exceeding 30 c.m.³ becomes necessary—the amount required to bring out the rose colour in blank tests containing no gold. After the introduction of 0.1 c.m.³ of N/1000 iodine into a mixture of potassium iodide and starch indicator of volume not exceeding 30 c.m.³, a single drop of the gold solution—equivalent to 0.000002 grm. of gold—gave a distinct rose colour; before such adjustment of the solution five drops—equivalent to 0.000010 grm. of gold—were needed to develop the same colour.

These results run on the whole as regularly as could be expected, and the use of the dilute standard solutions is obviously of advantage.

In the practical application of any such process for the determination of gold, the elementary form of that metal is the natural starting-point. To get the metal into solution with chlorine water or mixed hydrochloric and nitric acids is an easy matter, but the removal of the excess of the oxidiser by evaporation without reducing some auric chloride to the aurous form is difficult. We have found, however, that the free chlorine may be removed from a solution of auric chloride, without reducing the auric salt, by treatment of the solution with ammonia in excess, boiling gently, acidifying with hydrochloric acid, and heating if necessary to re-dissolve the precipitate by ammonia, again treating with ammonia and heating, and once more acidifying. On the second addition of ammonia no precipitation usually takes place with the amounts of gold which we have thus handled, perhaps because enough ammonium chloride has been found to hold it up.

The following table contains determinations made with such a solution of pure gold leaf—tested gravimetrically as to purity.

TABLE III.

Gold chloride made by dissolving 0.0104 grm. of pure gold in the manner described and diluting to 200 c.m.³.

Sodium thiosulphate, nearly

N/1000 = 0.17012 to 1 litre.

Iodine, nearly N/1000 = 0.13697 " "

Potassium iodide = 10 grms. " "

(Portions were treated with the potassium iodide without previous dilution).

	AuCl ₃ taken. C.m. ³ .	KI taken. Grm.	Na ₂ S ₂ O ₃ used. C.m. ³ .	Gold taken. Grm.	Gold found. Grm.	Error. Grm.
1.	1	0.005	0.55	0.000052	0.000058	+0.000006
2.	1	0.005	0.55	0.000052	0.000058	+0.000006
3.	2	0.005	1.06	0.000104	0.000112	+0.000008
4.	2	0.005	1.08	0.000104	0.000114	+0.000010
5.	5	0.01	2.45	0.000260	0.000260	0.000000
6.	5	0.01	2.50	0.000260	0.000265	+0.000005
7.	5	0.01	2.45	0.000260	0.000260	0.000000
8.	5	0.01	2.50	0.000260	0.000265	+0.000005
9.	5	0.01	2.50	0.000260	0.000265	+0.000005
10.	10	0.02	4.86	0.000520	0.000515	-0.000005
11.	10	0.02	4.85	0.000520	0.000517	-0.000003
12.	10	0.02	4.90	0.000520	0.000520	0.000000
13.	10	0.02	4.80	0.000520	0.000512	-0.000008
14.	10	0.02	4.84	0.000520	0.000516	-0.000004

Obviously, this method, which rests upon the hypothesis that sodium thiosulphate acts in the normal manner

only upon the iodine set free by the interaction of gold chloride and potassium iodide, offers trustworthy means for the determination of small amounts of gold.

NOTICES OF BOOKS.

A Short History of the Progress of Scientific Chemistry in our own Times. By W. A. TILDEN, D.Sc., F.R.S., Professor of Chemistry in the Royal College of Science, London. London: Longmans, Green, and Co. 1899. Pp. 276.

THE volume now before us is the outcome of a series of "Lectures to Working Men" given by Prof. Tilden in the sixtieth year of the Queen's reign. He took as his subject the progress made in the science and practice of chemistry during the preceding sixty years, and he showed how the present system of chemistry has been built up from the previously existing order of things.

At the commencement of the Queen's reign, Liebig's influence and teaching was beginning to be felt, and the new organic chemistry was attracting attention.

The author first deals with matter and energy, and draws attention to the two important principles, viz., the conservation of matter and the indestructibility of energy, and the work done by Newton, Rumford, Davy, Joule, Boyle, &c., on these subjects. The chemical elements, their distribution in nature and recognition by the chemist, are next discussed. The recognition of an element does not necessarily imply, as is often supposed, the isolation of the element itself. Fluor-spar, for instance, was known as far back as the middle of the last century to yield an acid analogous to hydrochloric acid, but the element fluorine was not isolated until Moissan achieved this result in 1886. In the same way alumina was known as a distinct earth in 1754, but the metal was not isolated until Wöhler obtained it in 1828. Since the year 1837, when only 54 elements were known, there has been, and still is, a steady augmentation of the number recognised as such, and in 1897 their number was nearly 80.

The atomic theory was first applied to chemistry by Dalton, but he was obliged to admit later on that his simple hypothesis of single atoms joining to form compound bodies was not applicable to all cases, and was opposed to well-established facts; it served, however, as a starting point for the now fully-developed theory.

In Chapter V. the author considers the origin and development of the ideas of valency and the linking of atoms.

The first important step in this direction was made by Gerhardt, and adopted by Laurent in 1842. According to this system the formula of each substance represents that quantity of it which, in the state of vapour, would occupy two volumes, the unit volume being the space occupied by one part by weight of hydrogen gas at standard temperature and pressure. The next important step was taken by Würtz in 1849, when, while studying the action of potash on cyanic and cyanuric ethers, he was led to the discovery of the compound ammonias; Würtz regarded ammonia as a link between inorganic and organic chemistry. The development of synthetical chemistry is dealt with in Chapter VI. This subject has made remarkable strides of late years, and, as the author points out, has now reached the borderland where chemistry and physiology meet.

Stereo-chemistry (Chapter VII.), or chemistry in three dimension, is founded on the ideas expressed by Pasteur in general terms, though the original discovery of right and left-handed polarisation was made by the French physicist, Biot. The fundamental idea of stereo-chemistry, however, arises immediately out of the doctrine of atoms. In this subject the names of van't Hoff, Le Bel, Kekulé, and others are well known. Chapter IX. is devoted to

discoveries relating to the liquefaction of gases, a subject sufficiently fresh in our memories not to require more than a passing notice.

We must congratulate the author on the excellent manner in which he has reviewed the subject of the progress of chemistry, a subject so vast as to cause considerable hesitation as to what to take and what to leave; he has, however, steered the middle course, and while not giving much time to the older and exploded doctrines, he has pointed out the influence they have had on our more modern and fully-developed ideas, the greatest of which is the atomic theory, without which organic chemistry would simply be a mass of confusion.

Introduction to Chemical Technical Analysis. By Prof. F. ULZER and Dr. A. FRAENKEL. Authorised translation, with appendix by the translator, HERMANN FLECK, Nat. Sc.D. Illustrated. Philadelphia: P. Blakiston, Son, & Co. London: Kegan Paul, Trench, Trübner, & Co., Ltd. Pp. 188.

THE value of manipulative skill cannot be over-estimated in chemical analysis; it is therefore important to give students as wide an experience as possible, with special instruction in carrying out the methods employed in the analysis of industrial products. The authors of this book have had much experience in teaching technical chemical analysis, and have therefore been able to give many methods of this description in a series of examples selected from a variety of products.

It is assumed that the student is already fairly well qualified as an analyst, all the examples given in this volume being special methods for individual cases. They include products of and materials used in technical chemistry, such as pyrites, sulphuric acid, brine, hydrochloric acid, soda, Weldon mud, furnace gases, &c.; cement and clay, the raw materials for the products of which are limestone, marl, and clay; the metallurgical industry; alloys and fertilisers; all of these being examples of inorganic analysis.

In organic analysis we find examples in the sugar industries; fermentation; fats, waxes, and oils; mordants and tanning materials; textile and dyeing industries; and the products of the coal-tar industry.

In the appendix, which has been added by the translator, there are a few special methods given for the analysis of white paint (white-lead), manganese dioxide, bleaching lime, &c.; asphalt and food stuffs, such as milk, butter, flour, tea, &c.

We must call special attention to a note on page 7, in which it is stated that in all temperatures $C = \text{Celsius}$, unless otherwise indicated. We think this is unfortunate, as C is always understood to mean centigrade in England, Celsius being practically unused, and not conveying much meaning to the majority of chemists. The book is well printed, and should be a useful addition to the library of the commercial analyst.

CORRESPONDENCE.

RELATIONS BETWEEN THE ATOMIC WEIGHTS AND PHYSICAL PROPERTIES OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—When the apparent equal expansion of gases was first observed, it was thought that if 273 volumes of a gas were taken at 0°C. , at -273°C. there would be no volumes of gas, or at any rate they would be in a state in which there was no molecular activity. I have, there-

fore, written absolute zero, understanding an, at present, theoretical state when all molecular activity has ceased.

Mr. Bayley, in his letter of last week, takes exception to my "assigning a positive value to zero in one instance or the other." But consider the case of any two elements, say hydrogen and iron. In the state which is to us normal, hydrogen is a gas and iron a solid. To get hydrogen into the solid state we have already to apply to it several hundreds of degrees of cold. If then we take these two solids and wish to get them to the state of absolute zero, we must in each case lower the temperature by a range in some way proportional to the atomic weights. So that in the case of these two elements we have—

Absolute zero for iron $\propto$ atomic weight.

Absolute zero for hydrogen $\propto$ atomic weight $\div$ number of degrees necessary to reduce it to the same molecular state as the iron; or generally

Absolute zero $= (c \times \text{at. wt.}) \div n$;

where n is the number of degrees necessary to reduce the element to the same molecular state as the "scratch" element.

Mr. Bayley further remarks that "it must not be overlooked that boiling-points, unless taken in an absolute vacuum, must be arbitrary." That any boiling-point could have a positive value I would not assert, but if the boiling-points under discussion were all taken under the same pressure the results can be compared with fairness.

To speak of taking a boiling-point in absolute vacuum must be a slip of the pen on Mr. Bayley's part, as by the definition of a boiling point, one such point under these conditions would be impossible, for by the term absolute I understand that the vapour given off by the substance itself is also withdrawn.

This he has himself shown in his paper of the same issue on "The Relation between Boiling-point and Melting-point in the Hydrocarbons," adding that if a substance in absolute vacuum be placed near a source of heat the temperature will rise in a certain way. This might be so if it could be explained how heat may be transmitted through an absolute vacuum; and even then the boiling-point is not dependent on the temperature, but on the pressure. If an absolute vacuum could be obtained, a lump of iron placed therein would boil, according to the definition. Thus, even if heat could be transmitted through an absolute vacuum, what Mr. Bayley terms "intrinsic boiling-point" concerns the intermolecular state, but not the boiling-point.—I am, &c.,

ALFRED WERTHEIMER.

Stirling Chemical Works, Stratford, E.
January 9th, 1900.

PHYSICAL EQUILIBRIUM OF MOLECULAR SYSTEMS.

To the Editor of the Chemical News.

SIR,—In the address of Sir W. Roberts-Austen, delivered before the members of the Iron and Steel Institute, on May 4th, 1899, the following words occur:—"We must not lose sight of these relations of carbon and iron which involve physical equilibrium. Even the astonishing association of iron and carbon monoxide, in the volatile gaseous compound, with which the distinguished name of Mond is connected, affords a veritable triumph for dynamical chemistry. It is generally supposed that ozone is dissociated at 160°C. , but Dewar has devised a beautiful experiment to prove that ozone has two centres of stability, and one of these is near the melting-point of platinum (*vide* "Year-book" of Royal Institution of Great Britain, 1887-9, p. 559). It seems to be the same with the relationship of hydrogen and iron. We have recently learned that iron and hydrogen appear to be completely dissociated at 800°C. , and yet the same iron heated to a

still higher temperature, say 1200° C., will still yield hydrogen."

Silicon hexchloride (Si_2Cl_6) is, I believe, another example of this "double centre of stability" alluded to in the above.

According to the Text-books, "Silicon hexchloride (Si_2Cl_6), a colourless liquid which boils at 146° C., has a vapour which is perfectly stable below 350° C.; beyond that temperature the molecule gradually breaks down, until at 800° C. the compound is completely decomposed. If, however, the temperature of the vapour be suddenly raised from below 350° to above 1000° C., curiously enough we find no decomposition has taken place." We have, therefore, to deal with a compound stable below 350° and above 1000° C., but yet incapable of existing between these temperatures.

This cannot be explained by the hypothesis advanced by Dewar to account for the formation of ozone from heated oxygen gas, namely, the dissociation of the oxygen molecule into atoms, which unite on cooling to form ozone.

Can any of your readers give any other instances of similar phenomena, or advance any theory to account for the behaviour of silicon hexchloride?

The following occurred to me as a possible explanation:—

Let us assume that the molecule of a stable vapour is a system in a state of harmonious motion, and not a mass of atoms in discord, or, in other words, that the molecule is held together more by a certain correlation or harmony in the times of vibration of the atoms than by any very strong internal atomic attractions. It may easily be conceived that as the temperature increases, the mode of motion of some of the atoms in the molecule gradually becomes incompatible with that of neighbouring atoms, and thus discord and jarring is introduced. The atoms in the molecule no longer stir clear of each other.

In a word the atoms are now "Out of Time." Consequently the molecule becomes unstable and breaks up. At a still higher temperature the motion of the atoms in the molecule may be so altered that there again exists a harmony in their periods or modes of vibration. The atoms then cease to hinder and check each other, and thus settle down in a state of harmonious motion and consequent stable equilibrium. The atoms are now again "In time" and the molecule is stable.—I am, &c.,

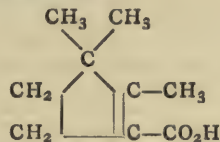
GEOFFREY MARTIN.

13, Hampton Road, Bristol.
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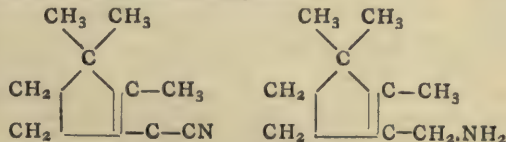
evolved, recognised by its odour. However, if the permanganate is added cautiously and not in excess, the decolouration is produced with no evolution of CO_2 . In this case only the group CH_2OH is attacked and transformed into CO , so as to produce oxalacetic acid, $\text{HO.CO}-\text{CH}_2-\text{CO}-\text{CO.OH}$. This acid can be recognised by the property it possesses of forming an insoluble mercury compound, not with the sulphate but with the acetate.

Acidimetry.—Henri Imbert.—In a previous paper the author mentioned that phenolphthalein admits of showing a feeble acidity, but a strong basicity, and inversely heli-antine, a strong acidity and a weak basicity. He now extends his researches by means of these two indicators, adopting the following order:—Acidimetry of (1) phenols, (2) monobasic fatty and aromatic acids, (3) halogenated monobasic acids, (4) nitrated monobasic acids, (5) alcohols or phenols of monobasic acids, (6) pluriphenolic monobasic acids, (7) amines of monobasic acids.

Amines enclosing the Camphor Radicle.—G. Blanc.—The comparative study of isolauronic and β -campholenic acids, and chiefly the consideration of their products of oxidation, shows clearly that there exists between them the same relation as that which exists between benzoic acid and phenylacetic acid.



If this relation is true it is easily seen that the partial reduction of isolauronic nitrite ought to give a base identical with β -amino campholene.



However, this reduction does not easily take place. The author investigates the various substances formed.

Allotropy of Benzophenone.—M. Gschner de Coninck.—Benzophenone presents two allotropic modifications, as was shown by Th. Zincke, but little is known about the conditions of transformation of the stable into the unstable variety. The author's researches show that, if he has not allotropised benzophenone by dissolving it twice in alcoholised water, slow oxidation, prolonged a sufficient time, should be stated amongst the conditions which allow of the transformation of the stable into the unstable variety of benzophenone.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 1, January 2, 1900.

Manganic Oxidation of Citric and Malic Acids.—G. Denigès.—When a cold solution of citric acid is treated with potassium permanganate, the mixture becomes brown very rapidly with effervescence, and then gradually becomes colourless. The gas escaping is CO , showing that the point of least resistance of the citric acid is attacked. $\text{HO}-\text{C}-\text{CO.OH}$ is transformed by oxidation into the ketonic group CO , with the simultaneous evolution of CO and water. To identify this compound the author utilises the property which the ketone has of giving with mercuric sulphate a compound insoluble in water. In the case of malic acid, when this acid is treated hot with a sufficient quantity of KMnO_4 , in addition to the colorisation of the reagent, ordinary aldehyde is

Bulletin des Travaux de la Société de Pharmacie de Bordeaux, September and October, 1899.

These two numbers contain no matter of chemical interest.

November, 1899.

A New Method for the Detection and Estimation of Small Quantities of Iodoform.—G. Denigès.—The author found that by heating an ammonia compound of the aromatic series with iodoform, he was able, thanks to the easy dissociation of this latter body under the influence of heat, to join the amine both to the methanic group $\text{H}-\text{C}\equiv$ and the acid radical I , necessary to form a salt of rosaniline, of which the intensity of the colouration enabled him to detect traces only of iodoform. He tried a large number of aromatic ammonia compounds, and obtained better results with the substituted amines in

amidogen than when the substitution took place in the nucleus. In practice two cases may present themselves; 1. The iodoform may be separated by ether from the substances with which it is mixed. 2. The iodoform may be in a solvent miscible with ether, and cannot therefore be isolated by its help. In the first case the ether is evaporated in a crucible, and 3 or 4 drops of dimethylamine, which was found to give the best results, added; if there is even only a trace of iodoform present, the mixture immediately takes a very distinct yellow colour. The liquid thus obtained is placed in a small test-tube, and heated nearly to boiling for a few moments only; on cooling, a little alcohol is added, and a liquid is obtained which appears red by transmitted and violet by reflected light if much iodoform is present, and violet only when there is only a small quantity of iodoform. In the second case 4 or 5 drops of the material—iodoformed galacol (for instance)—are put in a tube with an equal quantity of dimethylamine; the mixture takes a yellow colour, the intensity of which is in proportion to the quantity of iodoform present; on carefully heating the mixture and diluting with alcohol the violet colour is produced.

Contribution to the Study of the Products of the Oxidation of Morphine.—A. Loubiou.—Having occasion last year to prepare some oxydimorphine, the author tried the method of Polstorff and Brokmann; this method being so slow, and the difficulty of purification being so great, he was led to try and devise a more rapid method. He tried some experiments with peroxide of hydrogen and binoxide of lead, and obtained a very white and well-crystallised product with the former. The return by this new process is less than that with ferricyanide, but the product is obtained pure immediately; further, the operation does not take more than an hour to perform.

MEETINGS FOR THE WEEK.

- MONDAY, 22nd.—Society of Arts, 8. (Cantor Lectures). "The Nature and Yield of Metalliferous Deposits," by Bennett H. Brough.
- TUESDAY, 23rd.—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
- WEDNESDAY, 24th.—Society of Arts, 8. "Local Government and its relation to Parish Water Supply and Sewerage," by W. O. E. Meade-King, M.Inst.C.E.
- THURSDAY, 25th.—Royal Institution, 3. "The Senses of Primitive Man," by W. H. R. Rivers, M.A., M.D., &c.
- FRIDAY, 26th.—Royal Institution, 9. "Motive Power—High Speed Navigation—Steam Turbines," by Charles H. Parsons, M.A., F.R.S., M.Inst.C.E.
- Physical, 5. "Some Developments in the use of Price's Guard Wire in Insulation Tests," by Prof. Ayrton and Mr. Mather. "Reflection and Transmission of Electric Waves along Wires," by Dr. E. Barton and L. Lownds. "The Frequency of the Transverse Vibrations of a Stretched India-rubber Cord," by T. J. Barker.
- SATURDAY, 27th.—Royal Institution, 3. "Neglected Byways in Music" (with Musical Illustrations), by Sir Hubert H. Parry, Mus. Doc., M.A., D.C.L.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2096.

THE ESTIMATION OF INDIGO BLUE AND INDIGO RED IN NATURAL AND SYNTHETICAL INDIGOS.

By W. F. KOPPESCHAAR.

Of all the methods used for the estimation of indigo, the colorimetric method is the best, but only when the material contains no other colouring matter. In the opposite case, the solution obtained by treatment with concentrated sulphuric acid, diluting, and filtering, has a dirty appearance when contrasted with the pure solution of indigotine in the colorimeter.

In the method of titration by permanganate, we can never be certain that the impurities have not been oxidised at least partially. Further, the exact termination of the reaction is difficult to observe, and finally, if the sample contains a notable proportion of indigo red, the method is no longer applicable.

In the same way, in the determination of the oxygen necessary to oxidise a solution of white indigo prepared by reduction by means of hydrosulphite of soda, ferrous sulphate, grape sugar, &c., we cannot be certain whether the indigo is completely dissolved or whether the other substances do not also absorb oxygen.

As a consequence of the new methods of production, indigo (as well from Java as that from India) now contains more indigo red than it did formerly. Synthetic indigo red is now generally employed, but it is not identical with natural indigo red, and contains about 25 per cent of indigotine. The carmine from synthetic indigo red is easily soluble in concentrated solutions of chloride of sodium, while that from natural indigo is practically insoluble.

The method proposed by the author for the estimation of indigo blue and indigo red depends on the solubility of red and brown indigo in glacial acetic acid; blue indigo is insoluble in this reagent.

0.5 gm. of the finely-powdered sample is heated on the water-bath with 100 c.c. of glacial acetic for about an hour, in a conical flask of 8 or 9 c.m. diameter; the flask is then left in an inclined position, the liquid just reaching the neck, until all the insoluble matter is deposited. The clear liquid is then poured on an asbestos filter, prepared by placing a quantity of coarsely ground pumice-stone in a glass funnel up to 1 c.m. of the top, and covering this with a layer of asbestos. Care must be taken in decanting to leave the greater part of the insoluble residue at the bottom of the flask. The intensity of the colouration of the filtered liquid shows immediately whether the sample contains much or little indigo red.

In the latter case, a fresh quantity of acetic acid is added to the contents of the flask, and, after standing, decanted on the same filter. If, on the contrary, the sample is poor in indigo red, the small quantity that remains in the flask will not interfere with the ultimate estimation, and the washing may be omitted.

The asbestos and the pumice-stone, which shows whether any indigo blue has passed over, are removed from the funnel. This latter is placed stem upwards on the flask, so that its contents fall into the flask, and it is finally washed with 50 c.c. of pure sulphuric acid. After heating for two hours at 70°, and shaking frequently, the indigo blue is completely sulphurised. The solution is then poured into a 250 c.c. flask, and filtered after having been made up to that volume with water: 25 c.c. of the filtrate are diluted to 500 c.c., and the indigo blue determined colorimetrically by comparison with a solution

containing 0.1 gm. of pure indigotine per litre. This pure indigotine may be prepared by digesting pure indigo with acetic acid on a filter of hard paper and drying.

To estimate the indigo red, 5, 10, or 25 c.c. of the acetic solution is neutralised with caustic soda. For 5 c.c. we require 12 c.c. of a 20 per cent solution of soda. After standing for fifteen minutes, the precipitate is collected on a small filter and washed with a 5 per cent solution of soda to remove the indigo brown, then with 2 per cent acetic acid to neutralise the soda with which the filter is impregnated. After drying, the filter is shaken up with glacial acetic acid in a 50 c.c. flask and the colour of the solution is compared with that of a solution containing 0.05 gm. of pure indigo red in 1 litre of glacial acetic acid.

The pure indigo red is obtained from indigo, and purified first by the method described above, and then by sublimation at reduced pressure.

For the estimation of indigo red in the synthetic product containing indigo blue, only 0.1 gm. is taken. The accuracy of this method depends on the sight of the operator. The observations made by the author showed differences varying from 0.2 to 0.8 per cent with indigo blue, and much smaller ones with indigo red.—*Zeitschr. Anal. Chem.*, 1899, xxxviii., [1], p. 1.

A METHOD FOR THE ESTIMATION OF FERROCYANIDES IN OLD PURIFYING MATERIALS.

By E. DONATH and B. M. MARGOSCHES.

THE estimation of ferrocyanides is an operation which has often to be done by commercial chemists engaged either in the manufacture of prussiate both by the old process from residues rich in nitrogen and potash, a process which is gradually being abandoned, and by the new process which is now being adopted, the starting-point of which consists of exhausted purifying materials.

Some time ago Zulkowsky (*Dingl. Polyt. Journ.*, 1883, 249, 68) described a volumetric method for estimating the return in ferrocyanide of the melted mass by the old process. There are also several methods known for the estimation of the Prussian blue in old purifying material (C. Moldenhauer and W. Leybold, *Journ. f. Gasbel.*, 1889, 155; Knublauch, *ibid.*, 1889, 450; Gasch., *ibid.*, 1889, 166; Drehschmidt, *ibid.*, 1892, 221).

Frequent analyses of old purifying material have made us endeavour to find a more rapid method, which would at the same time be as exact, for the estimation of ferrocyanides besides those already published.

The method we have devised rests on the following facts:—The alkaline ferrocyanides, as well as the ferricyanides, in acid solution, energetically resist the action of oxidising agents even when these are fairly strong, while they are easily decomposed by the same reagents in alkaline solution. Under these conditions all the iron is separated in the form of a precipitate composed principally of ferric oxide, and is easy to estimate quantitatively.

When we place in contact a solution of potassic ferrocyanide and bromised soda, at the ordinary temperature (80 grms. of sodic hydrate is dissolved in water, and after cooling made up to 1 litre, 20 c.c. of bromine are then added while stirring vigorously) no reaction takes place; but, after prolonged heating, a thick pulverulent heavy precipitate, of a brick-red colour, is formed, and at the same time there is a lively disengagement of gas.

Qualitative analyses have shown that in this reaction the ferrocyanide is first transformed into ferricyanide, and this latter, being submitted in its turn to oxidation, is decomposed in the manner just described. The reaction therefore has two phases. On leaving the precipitate

formed to stand for some hours, then filtering and washing it, the iron can be estimated by any well-known method, and the proportion of ferrocyanide present calculated. It suffices to multiply the weight of the iron found by 7.5476 to get the amount of the crystallised salt $K_2FeCyg + 3H_2O$, or by 6.5833 for the anhydrous salt.

The iron in this precipitate may be estimated by several different methods.

¶ The precipitate can be dissolved on the filter by means of dilute warm hydrochloric acid, and the iron precipitated in the hydrochloric solution by ammonia. We can also dry the precipitate on the filter; put as much of the precipitate as possible into a small flask, incinerate the filter, decompose the small quantity of ferric oxide with bisulphate of potassium, add it to the rest of the precipitate, and dissolve the whole in dilute sulphuric acid. It must then be reduced by zinc and titrated with permanganate.

The analyses made by us gave very concordant results. Supposing the product obtained contained 99.6 per cent of crystallised potassic ferrocyanide, the results we obtained by this process were from 0.2 to 0.4 per cent too low.

The bromised soda as an oxidising agent can be replaced by permanganate of potash in alkaline solution. When we submit a solution of potassic ferrocyanide and an alkaline solution of permanganate of potash to the action of heat, the latter body is rapidly reduced under these conditions; there is evidently formed a precipitate of hydrated peroxide of manganese, besides the precipitate referred to above, and containing a quantity of ferric oxide corresponding to the potassic ferrocyanide present. By continuing the addition of the permanganate until the red tint remains constant, and adding dilute hydrochloric acid and heating, this precipitate, as well as the excess of permanganate, is decomposed and chlorine given off. It suffices to drive off the chlorine by heat, to separate the iron from the manganese by the acetate method, in the sufficiently diluted solution, to wash and calcine the precipitate of manganiferous basic ferric acetate, and to estimate volumetrically by permanganate the quantity of iron present.

In every case the use of bromised soda is preferable, in spite of its higher price, as its action is much more rapid.

To apply the process just described to old purifying material, the following is the best manner of proceeding:—Old purifying material contains, besides ferrocyanides, sulphur and a considerable amount of non-volatile tarry products. To estimate the Prussian blue, or rather the ferrocyanides, the material should be finely powdered, and treated at a gentle heat with an excess of caustic potash at about 15 per cent, with a view to completely transforming the Prussian blue into ferric hydrate and ferrocyanide of potassium. After dilution, the alkaline liquid obtained is filtered and the residue washed, after having been treated on the filter with a small quantity of dilute potash lye, until the whole of the ferrocyanide has disappeared.

However, we eventually discontinued the use of this somewhat complicated and tedious method of decomposition, and adopted the method given by Cr. Moldenhauer and W. Leybold (*Fourn. f. Gasbel.*, 1889, p. 157).

The spent material is rapidly ground up in an iron mortar, well mixed, and 50 grms. is taken for the analysis. This sample is placed in a flask of 1 litre capacity, and moistened with 100 to 150 c.c. of caustic potash at 15 per cent. The flask is then left for some time in a warm place, and frequently shaken; it is then filled up to 1030 c.c., as the results obtained by the above-mentioned chemists show that the residue of 50 grms. of material occupies a volume of 30 c.c. The liquid is transferred to a larger flask, well mixed, and filtered through a folded filter-paper. The potassic ferrocyanide is estimated in an aliquot part of the filtrate, the colour of which varies from brownish-yellow to reddish-brown, by the method already described. We recommend, by preference, the

volumetric estimation of the iron in sulphuric solution by permanganate, after reduction to the ferrous state.

More exact results can be obtained by exhausting the material by means of sulphide of carbon, with the object of eliminating the sulphur and the greater part of the tarry products, previous to proceeding in the manner just described.

The analysis, by our method, of a particularly rich sample of an old purifying material, gave us the following results, calculated as crystallised ferrocyanide of potassium, 14.3, 14.54, 14.51, and 14.65 per cent; another method gave 14.48 per cent.

Although we have not had the opportunity of applying our method of analysis to the estimation of the ferrocyanides in the melted mass of the old process, we have no doubt but that, in this case also, this method would give entirely satisfactory results.

We may further mention that our method is not confined to the estimation of the ferrocyanide corresponding to Prussian blue, but it may also be used in connection with the ferrocyanides corresponding to the other hydroferrocyanic compounds which may be met with in all purifying material.—*Zeitschrift für Angewandte Chemie*, 1899, No. 15, p. 345.

THE TITRATION OF PERSULPHATES.

By MM. LeBLANC and ECKARDT.

THE discovery made by Marshall (*Fourn. Chem. Soc.*, lix., 771; *Mon. Scient.*, Nov., 1897, p. 818) of a practicable method for the preparation of persulphates, has given rise to a considerable amount of research on this class of bodies. According to Marshall, Elbs (*Fourn. f. Prakt. Chem.*, xlviii., 185; *Zeit. Elektr.*, i., 417; ii., 245; *Zeit. Ang. Chem.*, 1897, 195) and Schönherr were occupied with the electrolytic production of the persulphates and the study of their reactions. With regard to their physical properties these bodies were studied by Berthelot (*Comptes Rendus*, cxiv., 875), Löwenhertz (*Chem. Zeit.*, xvi., 838), Bredig (*Zeit. Phys. Chim.*, xii., 230), and Möller (*Zeit. Phys. Chim.*, xii., 555).

Persulphuric acid and its salts have already been used industrially, and are now beginning to be used in considerable quantities. It is, however, difficult to say at present whether the use of persulphate will be further developed, since the scientific study of these bodies is not yet complete.

However this may be, it is quite understood that at the present time it is a matter of great interest to find a simple method for the rapid estimation of the amount of active oxygen in a solution of a persulphate. With this object Marshall (*loc. cit.*), Löwenhertz (*loc. cit.*), Möller (*loc. cit.*), Elbs (*loc. cit.*) and Schönherr have already proposed adding to the persulphate an excess of a solution of a ferrous salt, and to titrate the excess with permanganate. None of these writers, however, have given any indication as to the method of working to be followed; they have all limited themselves to showing the accuracy of the method by check analyses made in a different manner. Poleck's remark (*Chem. Zeit.*, xx., 631), according to which it is necessary to add to 0.2 gm. of persulphate 4 to 4½ times its weight of the iron salt, appears to be somewhat strange.

Being occupied in the manufacture of persulphates and in measuring their powers of oxidation, we have had recourse to the methods in question, and we immediately met with certain difficulties. The salts we prepared showed nothing but an absolutely insignificant power of oxidation, not only in our own hands, but also in those of other chemists who undertook their analysis. Further, the results of the analyses were far from being concordant. We therefore decided to study the question much more closely, and we almost immediately discovered the cause of the anomaly. The reaction between the persulphate and

the salt of protoxide of iron only takes place very slowly at the ordinary temperature of the laboratory, which will explain the low results obtained. The error, in fact, may reach 20 or even 30 per cent. On the other hand, at high temperatures, we can easily obtain very exact results.

We will give a few examples which will quite clear up the question:—The salt decomposes according to the equation, $K_2S_2O_8 = K_2SO_4 + SO_2 + O_2$.

By the loss of weight, therefore, we can determine the value in persulphate of the sample analysed. Our results were as follows:—

1. 0.5995 grm. $K_2S_2O_8$ gave 0.3845 grm. of residue.
2. 0.6030 " " " 0.3865 " " "

If we admit, what is extremely probable, that the residue is formed entirely of sulphate of potassium, and that this sulphate exists in the state of persulphate in the original sample, it is easy to deduce that the proportion of persulphate in the salt analysed was 99.54 per cent according to the first analysis, and 99.50 per cent according to the second. It is evident that this salt was contaminated with a small quantity of persulphate of ammonia.*

We dissolved 2.474 grms. of persulphate, and made the volume of the liquid up to 100 c.c. For each titration we took 10 c.c. of this solution, to which we added 5 c.c. of sulphuric acid of 1.16 density. We then added an excess (1 to 10 c.c. too much) of a solution of the double sulphate of iron and ammonia (at 30 grms. per litre), and titrated the excess of iron by means of a solution of permanganate of potash at 2.4 grms. per litre.

Below we give a description of the different experiments made.

1. To the mixture prepared in the manner we have just described, we added about 100 c.c. of distilled water at 70–80°, then, without further heating, titrated with permanganate. The permanganate itself had already been titrated in duplicate by means of pure Mohr's salt, and with oxalic acid. The following were the results:—

(a) 24.67, (b) 24.60 c.c. of solution, which gave, for the solid salt analysed, (a) 99.71 per cent, (b) 99.79 per cent of pure persulphate of potash.

2. The preceding mixture was prepared in an atmosphere of carbonic acid; 100 c.c. of boiled distilled water are added, the whole heated to 60° and kept at that temperature for ten minutes. It was then titrated with permanganate. The results were as follows:—

(a) 24.66, (b) 24.65 of iron solution, which corresponds to (a) 99.68 per cent, (b) 99.63 per cent, of pure persulphate of potash in the original sample.

As can be seen from the first experiment, we obtain good results by raising the temperature, without driving off the air. The same result could not be obtained at the ordinary temperature except after a much longer time.

3. The same mixture was diluted with 100 c.c. of water and left in contact with carbonic acid at the ordinary temperature for half an hour. (Air produced exactly the same effect). The solution was then titrated with permanganate, and the following results obtained:—

(a) 24.62, (b) 24.60 c.c. of iron solution, which corresponds to (a) 99.51, (b) 99.68 per cent of pure persulphate of potash in the sample. On the other hand, by not taking any precautions, and operating in the presence of a variable excess of the ferrous solution, we obtained the following results:—

4. One c.c. of iron solution in excess, and titrating with permanganate as rapidly as possible. Result: 14.41 c.c. of iron solution = 58.25 per cent of persulphate.

5. Four c.c. of iron solution in excess, titrate rapidly. Result: 18.96 c.c. of iron solution = 76.66 per cent of persulphate.

6. Five c.c. of iron solution in excess, titrate rapidly.

* This method of estimation does not enable us to form any conclusion as to the oxidising power of the substance. If, for example, we mix 174 grms. of sulphate of potassium and 96 grms. of sulphate of ammonia, and submit this mixture to the examination in question, we could deduce a proportion of persulphate of potash present of 100 per cent, while the true quantity would be 0 per cent.

Result: 20.22 c.c. of iron solution = 81.74 per cent of persulphate.

7. Ten c.c. of iron solution in excess, titrate rapidly. Result: 22.32 c.c. of iron solution = 90.22 per cent of persulphate.

8. Twenty c.c. of iron solution in excess, titrate rapidly. Result: 23.60 c.c. of iron solution = 95.39 per cent of persulphate.

9. One hundred c.c. of iron solution in excess, titrate rapidly. Result: 24.64 c.c. of iron solution = 99.59 per cent of persulphate.

10. One hundred c.c. of iron solution in excess, titrate rapidly. Result: 24.60 c.c. of iron solution = 99.44 per cent of persulphate.

To sum up, the reaction is the more rapid the greater the excess of iron salt present, a result that could be foreseen according to the law of masses. It is also probable that the ferrous salt exerts a catalytic action. Poleck's observation is therefore not unreasonable; it is, however, much simpler to titrate warm, and thus avoid the large excess of the iron salt.

We have further endeavoured to find whether, instead of working at a high temperature, we could not make use of a catalytic material; but up to the present we have not obtained any favourable result. There is nothing to be expected from metallic salts, since the solution already contains iron and manganese in large quantities. Platinised asbestos, such as is used in the manufacture of sulphuric anhydride, has not given any result.—*Zeitschrift für Elektrochemie*, 1899, p. 355.

CONTRIBUTION TO THE ASSAY OF GOLD.

By W. WITTER.

Not long ago Bock (*Chemiker Zeitung*, 1897, p. 973, and 1898, p. 358), published a new method for the assay of gold, a method which had none of the disadvantages of the old process, while being quite as rapid. I have made a large number of experiments with a view to proving the accuracy of the old method, and to examine the advantages offered by Bock's new method. I proposed to decide the following questions:—1. The difference which exists between the commercial assay and scientific analysis; 2. Is cupellation, in our present state of knowledge, sufficiently exact to serve as a basis for commercial transactions? 3. Is an analysis of any practical use, from the point of view of loss of interest, in the case of large quantities of gold? 4. What advantages has Bock's method over the usual method? 5. How far can it be trusted?

In cupellation, temperature plays an important part.

According to Rose (*"Metallurgy of Gold,"* 1896, p. 441), there is a loss of 0.01 per thousand of gold for a rise of temperature of 5°. I have succeeded, with the help of a platinum-rhodium couple, and a Keiser-Schmidt galvanometer, in maintaining a constant temperature during the whole operation, and thus obtained results conforming to those given by wet analysis. For chemically pure gold, it is necessary to have a temperature of 960°, less fine gold requires 950–960°, and gold containing small quantities of platinum requires a temperature of 1000–1010°. Ductile gold, 973 fine, containing both silver and copper, requires practically the same temperature as chemically pure gold. Gold coin, containing 100 parts of copper to 900 parts of pure gold, should be heated to only 920–930°, while for gold only 720 fine, containing silver and copper, a temperature of 900° is even too high.

When a good pyrometer is not obtainable, alloys melting at temperatures varying by 20–25° from 850–1050 can be used.

The Franksfurter Scheideanstalt prepares these alloys. By this means very satisfactory results can be obtained, not differing more than 0.02 per cent or 0.2 per thousand,

With regard to questions 2 and 3, the variations noticed, 0.0-0.2 per thousand, are extremely small, and show that cupellation can well be used as a basis for commercial transactions.

The results obtained by Bock's method are a little higher, say 0.2 per thousand. Although the old method is sufficiently exact, Bock's process can, in certain cases, be employed with great advantage, above all when it is necessary to make a number of analyses of one and the same substance. This method requires less manipulative skill on the part of the operator than does cupellation, and temperature has no influence at all. Unfortunately it is up to the present only applicable to the assay of gold coin.—*Chemiker Zeitung*, 1899, p. 522.

THE ESTIMATION OF SULPHYDRIC, SULPHUROUS, AND HYPOSULPHUROUS ACIDS.

By W. FELD.

THE methods described in this paper are applicable to the alkaline or alkaline-earthly salts of the above mentioned acids, even when they are present in extremely small quantities.

1. *Sulphides*.—The alkaline or alkaline-earthly sulphides give up the whole of their sulphur as sulphuretted hydrogen when boiled with a concentrated solution of chloride of magnesium in an atmosphere of carbonic acid.

The powdered sample, moistened with water, is placed in a conical flask of 300 c.c. capacity, fitted with an india-rubber stopper with two holes. Through one hole passes the stem of a funnel, fitted with a tap, and reaching to the bottom of the flask; through the other hole passes the escape tube which leads the gas through four wash-bottles. The fourth bottle is connected to a 10-litre flask serving as an aspirator. The opening of the funnel is fitted with a cork carrying a tube connected to a source of carbonic acid. This carbonic acid should not have any action on a solution of iodine. The first wash-bottle is empty, the second and third contain a quantity of a solution of iodine, more than sufficient to absorb the whole of the sulphuretted hydrogen disengaged; and finally, the fourth wash-bottle contains a decinormal solution of hyposulphite, for the purpose of absorbing the traces of iodine which might be carried through the preceding bottles by the current of carbonic acid gas.

We begin by passing through about 1 litre of carbonic acid for the purpose of driving the air out of the apparatus. The top of the funnel tube is then closed, and the stopper taken out of the funnel neck; 20 c.c. of a 25 per cent solution of chloride of magnesium are then poured in, and the rubber stopper replaced, and, by opening the tap, the chloride of magnesium is run into the flask, which already contains the sample. Heat slowly to boiling, while continuously passing carbonic acid gas through at the rate of 10 litres in three-quarters of an hour. The operation is generally finished at the fifth litre. The wash-bottles are then disconnected, emptied, and carefully washed out with distilled water; the whole of the liquids are then added together and titrated as one.

The reactions are as follows:—

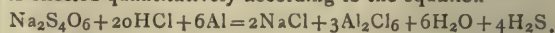
1. $\text{BaS} + \text{MgCl}_2 + \text{CO}_2 + \text{H}_2\text{O} = \text{BaCl}_2 + \text{MgCO}_3 + \text{H}_2\text{S};$
2. $\text{H}_2\text{S} + 2\text{I} = 2\text{HI} + \text{S}.$

2. *Sulphites*.—Proceed as for sulphides, but replacing the chloride of magnesium by hydrochloric acid.

3. *Hyposulphites*.—Hyposulphites give off a little sulphuretted hydrogen when treated with hydrochloric acid; the following is a method which gives exact results:—

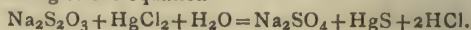
The hyposulphite is first transformed into tetrathionate by titration with a solution of iodine. The solution of tetrathionate, diluted with 50 c.c. of water, is placed in a flask with an excess of aluminium foil, and treated with dilute hydrochloric acid, in an atmosphere of carbonic

acid, in the cold. The reduction to sulphuretted hydrogen is effected quantitatively according to the equation—



4. *Hyposulphite in the presence of Sulphite*.—This estimation is made by method 3; the titration with iodine oxidises the sulphite into sulphate, which is not modified by nascent hydrogen.

5. *Sulphite in the presence of Hyposulphite*.—Add to the substance an excess of bichloride of mercury; the hyposulphite is thus transformed into mercuric sulphide according to the equation—



The sulphate is not modified by this reaction, and can be determined by method 2.

6. *Sulphide, Sulphite, and Hyposulphite*.—The sample is first treated with chloride of magnesium, as described in par. 1. In this manner the sulphide is estimated. The wash-bottles are refilled, and an excess of bichloride of mercury is then added to the contents of the flask, in the cold; then distil with hydrochloric acid, as described in par. 2. We thus obtain the sulphite. Finally, the hyposulphite is determined on a fresh portion of the sample, by titrating with iodine; the sulphide is thus transformed into sulphur, and the sulphite into sulphate. There now remains only the reduction by nascent hydrogen as described in par. 3.

If, besides the alkaline and alkaline-earthly salts enumerated above, the substance contains polysulphides, free sulphur, or sulphides of the heavy metals, the difficulties of titration are much greater, and have not yet been satisfactorily overcome. In the meantime, however, fairly good results have been obtained by the following method of procedure:—

The free sulphur is extracted with bisulphide of carbon and weighed after evaporating off the solvent. The sulphur present in the form of sulphide is then estimated by the method given in par. 1. In this operation the sulphur of the polysulphides is given off partly in the state of sulphuretted hydrogen, the remainder separating in the free state.

This latter portion is extracted with bisulphide of carbon. In any case, if the sample contains a sulphite, a little hyposulphite is formed. The solution is then titrated with iodine. During this operation the sulphur present in the state of ferrous sulphide separates in the free state, and can be extracted with bisulphide of carbon. The solution is then treated by method 3, to estimate the hyposulphites. Here the presence of other polythionic acids might introduce an error.

In solid substances, sulphites may occur in the presence of polysulphides; in such a case they are estimated by treatment with bichloride of mercury and distillation with hydrochloric acid, according to method 2.—*Die Chemische Industrie*, xxi., p. 372-380.

Estimation of Boric Acid in Boracite.—Dr. Rudolph Schwartz.—The disaggregation of boracite is effected in the following manner: 1 to 2 grms. of the finely powdered material are treated with 5 to 10 c.c. of hydrochloric acid at 1.124, and 100 c.c. of water, and heated for about twenty or thirty minutes on the water-bath in a flask fitted with a vertical condenser, and then left to stand for several hours. It is then filtered, washed thoroughly, and neutralised exactly by means of a N/5 solution of soda, in the presence of two or three drops of methyl orange. The solution thus obtained is poured into a 100 or 200 c.c. flask, and made up to the gauge mark with water; 50 c.c., equal to 0.2 or 0.4 grm. of material, are taken, this is diluted to 150-200 c.c., and titrated with an N/5 solution of soda in the presence of phenolphthalein. To more easily note the exact termination of the titration, that is the production of the red colouration, it is advisable to add 50-60 per cent of glycerin; this latter must of course be perfectly neutral, and must be carefully neutralised if necessary.—*Chemiker Zeitung*, 1899, p. 497.

ON THE
VOLUMETRIC ESTIMATION OF CERIU.*

By PHILIP E. BROWNING.

(Concluded from p. 31).

The Action of Arsenious Oxide upon Cerium Dioxide
(with WM. D. CUTTER).

THE fact that cerium dioxide is reduced by hydriodic acid suggested the possibility of the application of arsenious acid in acid solution to the same end, according to the reaction $4\text{CeO}_2 + \text{As}_2\text{O}_3 = 2\text{Ce}_2\text{O}_3 + \text{As}_2\text{O}_5$.

The extreme difficulty with which the ignited cerium dioxide when pure dissolves in acids has already been mentioned, and for this reason it was found practically impossible to obtain any results by this method. Weighed portions of the dioxide were placed in Erlenmeyer beakers with an excess of a solution of arsenious oxide $\frac{1}{10}$ N. 10 c.m.³ of (1:1) sulphuric acid were added, and the boiling continued until the fuming-point of the acid was reached; but even at this point only a partial solution of the dioxide had taken place.

The dark brown powder obtained by igniting the carefully washed oxalates, precipitated in acid solution by treating a solution of crude cerium chloride with ammonium oxalate or oxalic acid, is very fairly soluble in acids. Mengel (*Zeit. Anorg. Chem.*, xix., 67) has recently shown that this product contains a dioxide of praseodymium which acts as does cerium dioxide toward reducing agents. This fact makes the results recorded in the treatment of this ignited mixture of oxides of no value analytically, but of interest in the comparative study of the two reducing agents—arsenious oxide and hydriodic acid. Two portions of this mixture of oxides gave the following results, which agree fairly well with those of Mengel.

	Amount of substance taken.	$\text{CeO}_2 + (\text{PdO}_2?)$ found.	Calculated on 0.1000 gm.
	Grm.	Grm.	Grm.
1.	0.1037	0.0530	0.0511
2.	0.1034	0.0538	0.0520

The average of these results was taken as a standard—0.0515 gm. CeO_2 , &c., to every 0.1000 gm. of material. Three carefully weighed portions of this same material were placed in Erlenmeyer beakers with 10 c.m.³ of $\frac{1}{10}$ N arsenious oxide solution and 10 c.m.³ of dilute (1:4) sulphuric acid, and boiled until complete solution had taken place. The liquid was then cooled, neutralised with potassium bicarbonate, and titrated with standardising iodine to determine the amount of arsenious oxide remaining, and from it the amount used in the reduction of the dioxide according to the reaction given above. The results obtained follow.

	Amount taken.	Amount CeO_2 found.	CeO_2 calculated for 0.1000 gm.
	Grm.	Grm.	Grm.
1.	0.1005	0.0493	0.0491
2.	0.1015	0.0494	0.0487
3.	0.1005	0.0486	0.0484

As will be seen, the results obtained by this method fall about 0.0030 gm. below the standard as obtained by the distillation method, which seems to show that the arsenious oxide does not effect the complete reduction of the cerium dioxide from CeO_2 to Ce_2O_3 .

In order to study this point a little more fully and upon the pure dioxide, definite portions of a standard solution of pure cerium chloride were precipitated by ammonia in the presence of hydrogen dioxide and boiled to reduce the CeO_3 formed to the conditions of CeO_2 . The precipitated hydrated dioxide was filtered off and carefully washed until the washings gave no indication of hydrogen dioxide.

The moist precipitate was then washed into a beaker, 1 gm. of potassium iodide added, and 10 c.m.³ of strong HCl. The precipitate dissolved quite readily in the cold, and the iodine liberated was determined by standard sodium thiosulphate. The results appear in Table V.

TABLE V.

	CeO_2 taken.	CeO_2 found.	Error.
	Grm.	Grm.	Grm.
1.	0.1142	0.1140	0.0002—
2.	0.1142	0.1147	0.0005+
3.	0.1142	0.1152	0.0010+
4.	0.1142	0.1159	0.0017+
5.	0.1142	0.1152	0.0010+
6.	0.1142	0.1156	0.0014+

Another series of these precipitates prepared in the same way was boiled with a definite amount of arsenious acid in acid solution, as previously described in the case of the ignited dioxide. The results, which are recorded in Table VI., show, as in the case of the ignited dioxide, an insufficient reduction of the cerium by the arsenious acid.

TABLE VI.

	CeO_2 taken.	CeO_2 found.	Error.
	Grm.	Grm.	Grm.
1.	0.0381	0.0370	0.0011—
2.	0.0381	0.0361	0.0020—
3.	0.1142	0.1077	0.0064—
4.	0.1060	0.1002	0.0058—

The Estimation of Cerium Oxalate by Potassium Permanganate (with LEO. A. LYNCH).

Stolba (*Sitzungsber. d. kgl. böhm. Gesellsch. d. Wissenschaften*, iv., July, 1879; *Zeit. Anal. Chem.*, xix., 194) has stated that cerium oxalate may be estimated volumetrically after the same manner as calcium oxalate by treating the washed precipitate, suspended in warm water, to which a moderate amount of sulphuric acid has been added, by potassium permanganate. As the titration proceeds the precipitate disappears and the end-reaction is sharp. He also finds that the permanganate does not oxidise the cerium from the lower to the higher condition. So far as we have been able to discover, no experimental evidence has been presented to prove the correctness of Stolba's statement, and the work to be described was undertaken to furnish such evidence.

The solutions used were prepared and standardised as follows:—The cerium solutions were made by dissolving 10 grms. of pure cerium chloride in 1 litre of water, and standardised by precipitating measured and weighed portions in a faintly acid solution, with ammonium oxalate, filtering, washing, igniting, and weighing as the dioxide (CeO_2). A solution of potassium permanganate was prepared and standardised by titration against weighed amounts of ammonium oxalate. A solution of ammonium oxalate was made and its value determined by titrating measured amounts against potassium permanganate. Definite portions of the cerium solution were drawn from a burette and after diluting with water from 100 to 200 c.m.³ a definite amount of ammonium oxalate was added, care being taken to have an excess over the amount necessary, and the whole warmed to ensure a more crystalline precipitation. (As shown by the table, the precipitation was sometimes in neutral, sometimes in faintly acid solution). The precipitate was then filtered off on paper and carefully washed, the filtrate and washings being collected in a litre Erlenmeyer flask and set aside for future use. The precipitate was treated with about 10 c.m.³ of hot (1:4) sulphuric acid, which dissolved it completely, if not at first, by running it through the filter a few times, and the solution and washings were collected in another litre flask. The total volume of liquid was made up to about 500 c.m.³, warmed to about 70–80° C., and titrated with potassium permanganate to the appearance of the faint blush of colour showing the complete

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1899, vol. viii., No. 48.

oxidation of the oxalic acid. The filtrate from the cerium oxalate containing the excess of oxalic acid was diluted to 500 c.m.³, acidified with 10 c.m.³ of dilute (1:4) sulphuric acid, 1 grm. of manganous sulphate added to prevent the interfering action of the free hydrochloric acid upon the estimation of the oxalic acid (Gooch and Peters, *Am. Journ. Sci.*, vii., 461), and titrated with potassium permanganate after the same manner as the dissolved precipitate. A definite quantity of ammonium oxalate having been originally taken, it became possible, by subtracting from it the amount obtained, to derive the measure of the oxalate used in the precipitation of the cerium oxalate. By this procedure, it will be observed a check was made upon the results obtained by the titration of the precipitate. In Experiments 1 to 6 the cerium oxalate was thrown down in neutral solution, in Experiments 7 to 10 in acid solutions. The treatment of the filtrate in Experiment 1 was made without the presence of the manganous sulphate. The results recorded in Table VII. seem to uphold the statement of Stolba.

TABLE VII.

	Amount taken. Calculated as CeCl ₃ .	Amount found. Calculated as CeCl ₃ . of precipitate.	Error. Calculated as CeCl ₃ .	Amount found. Calculated as CeCl ₃ . of filtrate.	Error. Calculated as CeCl ₃ .
1.	0'1091	0'1087	0'0004—	0'1023	0'0068—]
2.	0'1091	0'1103	0'0012+	—	—
3.	0'1091	0'1087	0'0004—	0'1087	0'0004—
4.	0'1364	0'1373	0'0009+	0'1391	0'0027+
5.	0'1364	0'1367	0'0003+	0'1367	0'0003+
6.	0'2182	0'2202	0'0020+	0'2206	0'0024+
7.	0'1091	—	—	0'1087	0'0004—
8.	0'1519	0'1535	0'0016+	0'1535	0'0016+
9.	0'1364	0'1367	0'0003+	0'1367	0'0003+
10.	0'2182	0'2183	0'0001+	0'2183	0'0000

A CONTRIBUTION TO THE STUDY OF LIQUID MIXTURES OF CONSTANT BOILING- POINT.*

By GARNETT RYLAND.

(Continued from p. 16).

Methyl Alcohol and Benzene.

Method of Analysis.—The distillates were analysed by the following method:—

* From the *American Chemical Journal*, vol. xxii., No. 5, Nov., 1899.

Thirty to forty c.c. of the fraction boiling at a constant temperature were measured off into a burette and a definite proportion of water added. It was found that when alcohol constituted 30–40 per cent of the distillate the water added should be one-third of the volume of the sample. The burette was closed, shaken vigorously, and allowed to stand until the liquid within separated into two sharply divided layers of benzene and aqueous alcoholic solution. The volume of benzene could then be read off and its volume ratio to the alcohol converted into the weight ratio by determining the specific gravity of each liquid.

(The difference between the actual specific gravity of a solution of benzene in methyl or ethyl alcohol and that calculated from the specific gravities of the individual liquids was found by Paterno and Montemartini (*Gazz. Chim. Ital.*, 1894, xx v., II., p. 179) to be so small (1 or 2 in the third decimal place) that it may be disregarded in this method of determination).

A series of six test determinations of known mixtures gave the following results for the per cent of benzene by volume:—

	Per cent of benzene.					
	I.	II.	III.	IV.	V.	VI.
Calculated ..	58'8	59'5	59'5	60'0	64'0	64'0
Found ..	58'0	59'4	59'8	60'5	63'5	64'3

Results.—Methyl alcohol (distilled from lime at 64'5–65'0)* and commercial benzene (re-distilled at 79–79'5°) were mixed in the proportions, by weight, and distilled at the pressures given below. The constant boiling portions analysed were separated from the excess of either constituent by three fractional distillations in each case (see Table A).

Ethyl Alcohol and Benzene.

Mixtures of ethyl alcohol (distilled from anhydrous copper sulphate at 77'5–78°) and benzene (79–79'5°) were investigated, and it was found that a mixture containing about 32 per cent of alcohol was distilled to the last drop at 67–68°.

The results of the analysis of distillates under various pressures, obtained as in the case of methyl alcohol and benzene, are given in Table B.

To determine the percentage composition of the distillates, 40 c.c. were shaken with 50–60 c.c. of water.

Twelve analyses of known mixtures gave the following results for the per cent of benzene by volume:—

* The same thermometer was used throughout this and all succeeding investigations. It had been carefully tested, compared with two standard thermometers, and corrected. Whenever the pressure under which a liquid was distilled is not stated, it was approximately 760 m.m.

TABLE A.

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. M.m.	Boiling-point of fraction analysed.	Per cent of alcohol found.	Per cent of benzene found.	Ratio of products of vapour-tension by vapour density.*
I.	38 : 62	770	58°	38'4	61'6	At 60°, 37'8 : 62'2
II.	38 : 62	760	57'5–58°	39'0	61'0	
III.	37 : 63	400	40°	36'8	63'2	At 40°, 35'2 : 64'8
IV.	36 : 64	392	39'5°	35'7	64'3	
V.	41 : 59	223	25°	33'2	66'8	At 25°, 33'2 : 66'8
VI.	34 : 66	223	25°	33'1	66'9	

* See Berthelot and Thorpe, p. 16 (*ante*). The values for vapour-tensions throughout these investigations were taken from Landolt and Börstein's tables, Regnault's values being preferred.

TABLE B.

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. M.m.	Boiling-point of fraction analysed.	Per cent of alcohol found.	Per cent of benzene found.	V. t. × v. d. of alcohol V. t. × v. d. of benzene.
I.	33 : 67	769	67–68°	31'4	68'6	At 67'5°, 36'3 : 63'7
II.	33 : 67	763	67–68°	32'3	67'7	
III.	33 : 67	421	50–51°	28'2	71'8	At 50°, 32'3 : 67'7
IV.	28 : 72	423	50–51°	27'6	72'4	
V.	28 : 72	241	34'5–35'5°	23'3	76'7	At 35° 28'9 : 78'1
VI.	23 : 77	243	34'5–35'5°	23'4	76'6	

	I.	II.	III.	IV.	V.	VI.
Calculated ..	60.0	60.0	60.0	65.0	65.0	65.0
Found ..	59.9	59.9	62.2	65.2	64.8	65.0

	VII.	VIII.	IX.	X.	XI.	XII.
Calculated ..	65.0	70.0	70.0	70.0	75.0	75.0
Found ..	66.2	70.1	69.8	70.0	75.0	75.1

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 1st to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month was 1.30 inches. The average for the past thirty years is 2.10 inches; this leaves a deficiency of 0.80 inch, bringing the total deficiency for the year up to 4.54 inches, or 17.6 per cent, as will be seen by the following table:—

Rainfall in Inches at Oxford, Month by Month, during the Year 1899.

	Actual fall.	Mean of 30 years.	Difference from the mean.	
	Inches.	Inches.	Inch.	Inch.
January ..	2.85	2.16	—	+0.69
February ..	1.92	1.76	—	+0.16
March ..	0.25	1.50	-1.25	—
April ..	1.83	1.66	—	+0.17
May ..	1.37	1.83	-0.46	—
June ..	1.05	2.11	-1.06	—
July ..	1.32	2.68	-1.36	—
August ..	1.80	2.32	-0.52	—
September..	2.38	2.43	-0.05	—
October ..	2.59	2.75	-0.16	—
November ..	2.52	2.42	—	+0.10
December ..	1.30	2.10	-0.80	—
	21.18	25.72	-5.66	+1.12

During the month of December the bacteriological examinations of 502 samples gave the results recorded in the following table; we have also examined 34 other

Table showing the Average Monthly Bacterial Variations during the Year.

Month.	Thames, unfiltered.	Thames-derived Companies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London), filtered.	
January ..	22764	35	1651	11	4576	14	
February ..	23280	54	2995	19	7481	68	
March ..	12133	28	2032	35	3977	33	
April ..	10622	22	908	8	2490	5	
May ..	3247	26	430	15	1313	11	
June ..	1677	30	408	20	1225	19	
	12287	32	1404	18	3510	25	Mean of 1st 6 months.
July ..	1270	41	1858	30	4357	26	
August ..	2269	31	410	12	863	12	
September ..	574	16	170	4	220	9	
October ..	1367	20	290	10	876	21	
November ..	3724	11	355	13	513	7	
December ..	1883	14	387	4	590	10	
	1848	22	578	12	1236	14	Mean of 2nd 6 months.
	7067	27	991	15	2373	20	Mean of 12 months.

Averages of the Chief Chemical Composition of the Six Supplies derived from the River Thames.

	Common salt per gallon.	Nitric acid per gallon.	Hardness. Degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Colour. Brown : Blue.
January ..	2.236	1.032	15.73	0.072	0.227	25.4 : 20
February ..	2.144	1.107	15.75	0.073	0.207	26.6 : 20
March ..	2.092	1.014	16.14	0.037	0.134	12.5 : 20
April ..	2.147	0.932	14.43	0.031	0.093	8.8 : 20
May ..	2.235	0.868	13.67	0.036	0.102	11.5 : 20
June ..	2.150	0.724	13.40	0.033	0.095	10.5 : 20
July ..	2.150	0.623	13.04	0.035	0.085	10.2 : 20
August ..	2.202	0.756	13.00	0.035	0.086	13.8 : 20
September ..	2.174	0.677	13.08	0.032	0.083	14.5 : 20
October ..	2.198	0.638	13.85	0.028	0.084	11.9 : 20
November ..	2.439	0.771	14.85	0.058	0.155	24.0 : 20
December ..	2.432	0.884	17.01	0.036	0.132	19.9 : 20

samples, from special standpipes, &c., making a total of 536 samples:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	387
New River, filtered (mean of 24 samples) ..	4
Thames, unfiltered (mean of 24 samples) ..	1883
Thames waters, from the clear-water wells of eight Thames-derived supplies (mean of 270 samples)	14
Ditto ditto highest	154
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	590
River Lea, from the East London Company's clear-water well (mean of 36 samples) ..	10

The chief remark to be made with regard to the supply during December is to draw attention to the exceptional bacterial purity of the unfiltered waters of the Thames, New River, and the Lea. The general supply has been admirable from a bacteriological point of view.

During the past year we have examined 4792 samples of London water bacteriologically, as compared with 3500 and 3249 respectively in the two previous years. We have also made 2456 chemical analyses of London waters throughout this period, making a total of 7248 samples examined.

The accompanying table shows that during the first six months the Thames-derived Companies' clear water wells contained on the average 32 bacteria per c.c., while the New River and River Lea supplies contained respectively 18 and 25. During the second six months the number of bacteria in the waters from the three were respectively 22, 12, and 14. These results show that during the year effective filtration of the London waters has been properly maintained.

When we consider that a water containing about 100 bacteria per c.c. in the clear water wells would be regarded by the highest authorities as properly filtered, we see that the London supply must be considered exceptionally good.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

NOTICES OF BOOKS.

Inorganic Chemistry for Advanced Students. By Sir HENRY ROSCOE, F.R.S., D.C.L., LL.D., and ARTHUR HARDEN, Ph.D., M.Sc. (Vit.). With Fifty-four Illustrations. London: Macmillan and Co., Ltd. 1899. Pp. 432.

THE present work is intended as a Supplement to the smaller volume of "Inorganic Chemistry for Beginners," published six years ago, and is therefore for the use of students who have already had some practical experience in the Science. A useful feature of this book, which is not often met with in books for students, is a number of lessons on the application of chemistry to the Arts and Industries. These are interspersed throughout the volume, and come as a welcome relief to the tedium of a long series of lessons on the metals and their compounds.

Inorganic Chemical Preparations. By FELIX LENGFELD, Assistant Professor of Inorganic Chemistry in the University of Chicago. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1899. Pp. 57.

THIS manual was written for the classes in Inorganic Preparations at the University of Chicago, and is intended

for advanced students who are supposed to be able, at the end of the course, to make any inorganic preparation without assistance from an instructor. The methods given have all been verified, and found to give good results in the hands of a careful student. The student should first read and remember the general directions, and then, with ordinary intelligence, there is no reason why he should not be able to carry out all the methods and processes given; it will be advisable to begin at the beginning, and work steadily through as the preparations are given, not alphabetically or in groups, but in order of increasing difficulty.

At the same time book-work must not be neglected, as practice and theory go hand-in-hand, and mutually help one another. Numerous references to original articles are given throughout, and these should be looked up and studied.

Elementary Practical Chemistry. By MATTHEW A. PARKER, B.Sc., and D. R. BOYD, Ph.D., B.Sc. Glasgow and Edinburgh: William Hodge and Co. 1899. Pp. 82.

THE aim of the writers of this book has been to make it essentially a laboratory guide; it was written primarily for the author's own students, and is in most respects very similar to other books for beginners which are so constantly being published. To some extent the plan has been adopted of not fully describing the results to be obtained in a given experiment, but of leaving these to be determined by the student's own observation. We rather doubt the wisdom of this plan; most students require to be told what to expect, otherwise they are liable to be misled, or will not trouble to make sure that their results are what they should be.

A Treatise on Quantitative Electrolytic Chemical Analysis. ("Traité d'Analyse Chimique Quantitative par Electrolyse"). By M. J. RIBAN. With 96 Illustrations. Paris: Masson et Cie. 1899. Pp. 304.

EVERY day, quantitative chemical analysis by means of electrolysis acquires more and more importance; by its means delicate problems have been greatly simplified and taken into ordinary use, and, while giving a great increase in rapidity, it has not diminished the necessary accuracy.

The present volume contains the latest progress made in the science, and also gives a *resumé* of the present state of our knowledge of the subject; further, the author not only introduces the reader to electrolytic chemical analysis, but he also gives a practical guide to its daily uses.

The work is divided into four parts. The first part deals with early physical theories, definitions, laws, sources of electricity, measuring apparatus and its use, electrolytic apparatus, &c.; the second part is devoted to the individual estimation of the metals and metalloids by electrolysis; in the third part we find instructions for the separation of the metals one from the other by the same means; while part four is a collection of examples and methods to follow in complex general analyses, more particularly with regard to commercial products and minerals. A number of tables of measures and calculations relating to electrolysis complete the work, which is to be commended for great clearness of expression and style of printing. As is often the case, however, in French books, there is no index.

The Detection of Alkaline Chromates added to Milk as a Preservative.—Alex. Leys.—Fifty c.c. of the milk are evaporated to dryness in a porcelain crucible and calcined at a cherry-red heat; the ash is moistened with concentrated sulphuric acid; if chromates are present the sulphuric acid takes a reddish yellow tint, and a characteristic liberation of reddish fumes of chlorochromic acid is observed.—*Journ. de Pharm.*, x., No. 8.

CORRESPONDENCE.

OIL EXTRACTION.

To the Editor of the Chemical News.

SIR,—Having had occasion lately to make a large number of determinations of small quantities of oil, I have been considerably troubled by the difficulty of accurately weighing the comparatively large flasks generally used in extractions; errors, which in milk analysis are of little account, becoming serious when the substance to be weighed only amounts to a few milligrams.

To overcome this difficulty I have devised a special extraction flask, which is clearly shown in the accompanying sketch.



The ordinary flask of about 150 c.c. capacity is provided with a side tube fused on rather above the centre, and on to this side tube is ground a little weighing flask of about 10 c.c. capacity. The side tube projects a little way into the weighing flask, as shown.

The little flask is cleaned, heated in the water-oven, cooled, and weighed. It is then placed in position, and the large flask connected to the extractor as usual. At the close of the extraction the solvent is evaporated off until only enough remains to hold the oil in solution, and the large flask is then disconnected and slowly tilted until the residue runs into the little flask. If the little flask is then warmed, the large flask may be rinsed out by the condensed vapour of the solvent.

When the oil is completely transferred, the little flask is disconnected, heated in the water oven, and weighed.

The flask is of course equally applicable to milk or other extractions where accuracy is desired.—I am, &c.,

FRED. A. ANDERSON.

73, Queen Victoria Street, E.C.
January 17, 1900.

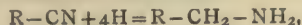
The Estimation of Persulphates.—G. H. Mondolpho.—This method consists in decomposing the persulphate by means of iodide of potassium, and titrating the iodine set free by means of hyposulphite. Two or 3 grms. of the sample are dissolved in 100 c.c. of water. 10 c.c. of this solution are treated with an excess of iodide of potassium (0.25 to 0.50 gm.), and heated for ten minutes to 60 or 80°. The iodine is then titrated with a decinormal solution of hyposulphite, using starch as an indicator towards the end of the reaction. The proportion of persulphate present is calculated from the equation, $M_7SO_4 + KI = M_7KSO_4 + I$. One c.c. of the hyposulphite solution corresponds to 0.114 gm. of NH_4SO_4 , and to 0.0135 gm. of KSO_4 .—*Chemiker Zeitung*, xxiii., p. 699.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

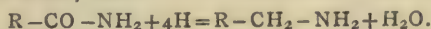
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal de Pharmacie et de Chimie,
Series 6, Vol. x., No. 4.

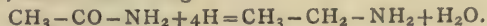
New Method for the Formation of Primary Amines.—M. Guerbet.—It has long been known that the nitriles change into amines possessing the same number of atoms of carbon, when treated with nascent hydrogen; the reaction is as follows:—



R being the monovalent radical. It appeared to the author that the amides might also be able to fix hydrogen, and change into the corresponding amines, losing 1 molecule of water, thus:—



This hypothesis has been verified by experiment, and the author has succeeded in partially transforming acetamide into ethylamine, by treating it with nascent hydrogen produced by the action of sodium on boiling amylic alcohol; the reaction being—



The method of procedure is as follows:—15 grms. of dry acetamide are dissolved in 600 grms. of amylic alcohol, previously distilled over caustic baryta, to remove all the moisture; 60 grms. of sodium are added, and the whole boiled until all the metal is dissolved. The gas given off, consisting of ammonia, ethylamine, and hydrogen, is passed through hydrochloric acid, which should remain acid till the end; it is then evaporated to dryness, leaving a residue composed of hydrochlorate of ammonium and hydrochlorate of ethylamine, which are easily separated one from the other by absolute alcohol.

On the Purification of Iridium.—E. Leidie.—Already inserted in full.

No. 5.

This number contains no matter of chemical interest.

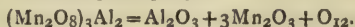
No. 6.

On Methylonylketone.—H. Carette.—An acetone obtained by the fractional distillation of essence of rue has been described as methylonylketone; the same body has also been obtained by the dry distillation of a mixture of cuprate and acetate of lime. With hydroxylamine the author has obtained an oxime which forms the subject of this note; the acetone used was obtained from commercial essence of rue. To obtain it in a state of purity it was combined with bisulphite of ammonia; the crystals thus obtained are insoluble in water, but very soluble in alcohol. Heated with water on the water-bath this bisulphitic compound is decomposed, giving pure methylonylketone. The boiling-point of this substance at 766 m.m. b.p. is 230°65', and at 0.24 m. b.p. it is 122°—123°. The oxime of this acetone was prepared by putting in contact equal molecules of hydrochlorate of hydroxylamine and methylonylketone,—that is, 21 grms. of hydrochlorate and 51 grms. of acetone; the strictly necessary amount of potash to decompose the hydrochlorate was also added, and a granular mass of butyrous appearance gradually separates. The reaction is greatly accelerated by the addition of enough alcohol to dissolve the acetone. When purified by crystallisation in dilute alcohol, methylonylketone-oxime appears in the form of elongated prisms, attaining a length of 6 c.m. It is insoluble in water, but soluble in alcohol, ether, benzene, chloroform, and toluene. The crystals are anhydrous and fuse at 46°.

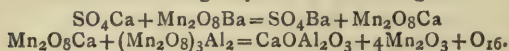
No. 7.

The Bio-chemical Purification of Waters.—M. Tixier.—Among the different substances which have been

proposed for the biological purification of waters, oxidising agents occupy a preponderating place, especially the permanganates. However, the various attempts made in this direction have all been nullified by reason of the impurities introduced by the reagent; for example, the use of permanganate of potash and lime gives rise to the presence of free alkali in the water, and small quantities of free lime (for that is the alkali present in most cases), make the water absolutely unfit for drinking purposes. This difficulty may be completely done away with by using permanganate of alumina and permanganate of baryta in variable proportions. The reactions which take place are as follows:—With waters free from sulphate of lime, for which only a small quantity of baryta would be necessary, we have principally—



With waters containing sulphate of lime we get—



The reactions take place easily in the cold, and the quality of a water can be determined five minutes after the addition of the first drop of the reagent; in some cases the reaction is instantaneous.

No. 8.

Reactions of Argon and Nitrogen on the Mercurial Radicals.—M. Berthelot.—The author's experiments were carried out under the influence of the electric discharge. Dimethyl-mercury, $(\text{CH}_3)_2\text{Hg}$, in the presence of argon decomposes, forming hydrogen, formene (or ethane, C_2H_6), and mercury. Analysis shows that no trace of argon was absorbed; on the contrary, the dimethyl-mercury absorbs nitrogen; 0.2576 grm. of dimethyl-mercury was operated on in a small bulb, the $\text{C}_2\text{H}_6\text{Hg}$ gave a gas, $\text{H}_2 + \frac{1}{2}\text{CH}_4$, with the absorption of 0.22 N_2 ; the composition of the condensed matter was therefore $1\frac{1}{2}\text{C} + \text{H}_3 + 0.44\text{N}$, that is $\text{C}_2\text{H}_3.4\text{N}^{0.50}$. Diphenyl-mercury does not easily lend itself to experiment on account of its solid state and the absence of any appreciable vapour tension at the ordinary temperature. However, after being submitted to the action of the electric discharge for twenty-three hours, the author found that 5.1 hundredths of the volume of argon was absorbed. The experiment was repeated on the gaseous residue with a fresh quantity of diphenyl-mercury, and after eighteen hours a further 3.8 hundredths were found to be absorbed.

Comparative Examination of some Rapid Methods for the Purification of Waters.—F. Malmejac.—This paper deals rather with mechanical than chemical action in the purification of water. The author has experimented on four processes, two using alum (Babés and Werner), and two using perchloride of iron (Almen d'Upsal and Manget). These processes are simple and rapid; the experiments show that the perchloride of iron processes give the best results, as they diminish the proportion of organic matter, either in an acid or alkaline medium, by 60 per cent, while the alum processes only reduce it by 25 and 33 per cent respectively. The two latter, however, have a stronger action—nearly three times as powerful—in destroying microbes.

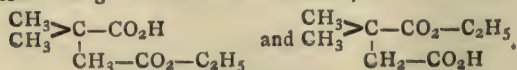
Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxi., No. 15.

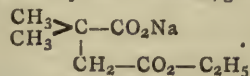
Decomposition of Carbonic Oxide in the presence of Metallic Oxides.—O. Boudouard.—Already inserted.

Decomposition of Carbonic Acid in the presence of Carbon.—O. Boudouard.—Already inserted.

The Synthesis of $\beta\beta$ -Dimethyl-levulic Acid.—E. E. Blaise.— $\alpha\alpha$ -Dimethylsuccinic acid being dissymmetric can give rise to two acid ethers,—

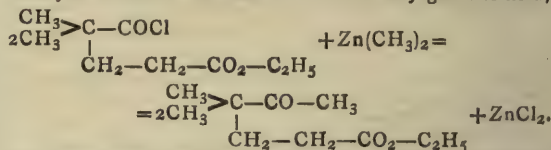


To obtain $\beta\beta$ -dimethyl-levulic acid, which is the same body as is formed by the oxidation of campholene, we must start with the first of these two acids. The author finds that the anhydride corresponding to $\alpha\alpha$ -dimethylsuccinic acid, treated with ethylate of sodium, gives an ether salt,—



He points out that while in the case of succinic anhydride a notable quantity of disodic succinate is precipitated, in that of its dimethyl derivative only traces of the neutral salt are formed. 30 grms. of the preceding acid ether and 26 grms. of trichloride of phosphorus are placed in a flask fitted with a vertical condenser, and heated gently on the water-bath at $60-70^\circ$ for 45 minutes. On cooling, the chloride ether of phosphorus anhydride is separated by decantation. Dimethyl-levulic acid, $\text{CH}_3 - \text{CO} - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CO}_2\text{H}$, is obtained by the action of zinc methyl on the preceding chloride ether. The product of the reaction is decomposed by water, and gives a benzenic solution from which the carbide is separated by distillation. The residue is fractionated *in vacuo*; the portion passing between $105-110^\circ$ at 20 m.m. is rectified, and then boils at $106-107^\circ$. This body is dimethyl-levulic ether; it is saponified with potash, acidulated with hydrochloric acid, and evaporated to dryness; the residue exhausted with ether yields to this solvent dimethyl-levulic acid, which may be purified by distillation *in vacuo*.

The Synthesis of $\gamma\gamma$ -Dimethylhexanonoic Acid, $\text{CH}_3 - \text{CO} - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}_2 - \text{CO}_2\text{H}$.—E. E. Blaise.—This acid has been obtained by the action of zinc-methyl on the chloride ether of $\alpha\alpha$ -dimethylglutaric acid,



Its ammoniacal salt has been prepared by passing a current of ammonia gas through an ethereal solution of the acid. It separates in the form of a crystalline precipitate, which when dry melts at $115-118^\circ$.

The Preparation of the Phenolic Chloro-carbonates.—E. Barral and A. Morel.—The authors have studied the action of COCl_2 on the phenols with two different objects: (1) to obtain neutral carbonates of chlorophenols, and to identify them with the products of direct chlorinisation of the carbonate of benzenol; and (2) to study the action of alcohols on the phenolic chloro-carbonates after having effected the same on the neutral phenolic carbonates and phosphates. They found that the more concentrated the alkaline phenate is, the more neutral carbonate is there formed; at too low a temperature the action does not take place; at too high a temperature (above 50°) the oxychloride decomposes, and with the most favourable conditions of concentration and temperature it is impossible to prevent the formation of the alkaline carbonate when using certain phenates, such as those of the naphthols and diphenols. In such cases the phenol is set at liberty, and very little symmetric carbonate and chloro-carbonate is formed.

On some Phenolic Chloro-carbonates.—E. Barral and A. Morel.—The authors have prepared the chloro-carbonates or chloroformates of benzenol, para-cresol, thymol, and galical, and they here describe their properties.

Action of Formic Aldehyde on Albumenoid Matters.—C. Lepierre.—The author finds that the *proto-albumoses* are rendered insoluble by warm CH_2O ; that the *dextro-albumoses* are not homogeneous bodies, but a collection of bodies formed of homologous units, the first of which, of a high molecular weight, are nearest to the *proto-albumoses*, and are rendered insoluble by CH_2O ;

the others, nearer the true peptones, are simply transformed into proto-albumoses, and are changed into insoluble derivatives by prolonged action of the reagent; and (3) the true peptones are first transformed into bodies of the dextro-class, and these again into proto-albumoses.

Cryoscopy of Butters and Margarines.—M. Pouret. —This method of examining butters for adulteration, though giving certain indications, is not sufficiently exact for practical purposes, the composition of different butters being so variable; in some cases as much as 15 per cent of margarine could be added without detection.

MISCELLANEOUS

A New Method for the Determination of Nitric Acid.—J. F. Pool.—The following method, according to the author, gives exact results for the estimation of nitric acid in potable waters, manures, &c. The sample is evaporated to dryness in an Erlenmeyer flask with an excess of chloride of sodium. The dry mass is decomposed by sulphuric acid in an atmosphere of carbonic acid, the mixture is diluted with water, and the chlorine driven off by boiling. The fumes given off are collected in a solution of iodide of potassium, and the iodine set at liberty is determined by titration. By operating, as has been said, in an atmosphere of carbonic acid, the binoxide of nitrogen set free according to the equation, $6\text{HCl} + 2\text{HNO}_3 = 2\text{NO} + 4\text{H}_2\text{O} + 3\text{Cl}_2$, is not transformed by oxidation, into products also capable of liberating iodine and passing into solution in the iodide of potassium.—*Nederl. Tijdsch. Pharm.*, xi., 171.

The use of Alkaline Solutions of Formic Aldehyde in Quantitative Analysis.—L. Vanino.—Gold can be estimated quantitatively by adding ordinary commercial formalin to a solution of the chloride, a few drops of caustic soda are then added and the whole heated for a few moments on the water-bath. The metallic gold is separated by filtration, and the filtered liquid is tested again by formalin to make sure that the precipitation is complete. The precipitated gold is washed with water, and then alcohol, and dried at 180° , or even heated to redness in a crucible. Silver can also be precipitated from its solution of nitrate by formalin, either in the cold or on a water-bath. In the latter case it is essential to wash the precipitate with absolute alcohol to remove the adhering water. Chloride of silver is reduced by formalin. This reaction can be applied, not only to quantitative analysis, but also to the preparation of pure silver from silver residues.—*Berichte*, xxxi. (II.), p. 1763.

Institute of Chemistry Examinations.—Pass Lists (January, 1900).—*Intermediate Examination*: F. W. Aston, Mason Univ. Coll., Birmingham; J. H. Austin, Mason Univ. Coll., Birmingham; H. J. Bailey, Univ. Coll., Sheffield; H. G. Bayly, King's Coll., London; G. Clarke, jun., Univ. Coll., Nottingham; M. W. Danks, Mason Univ. Coll., Birmingham; R. E. Blake Smith, B.Sc. (Lond.), Univ. Coll., London; Thomas Taylor, Glasgow and W. of Scotland Tech. Coll.; John Webster, Mason Univ. Coll., Birmingham; and W. E. Woodman, King's Coll., London. *A.I.C. Examination* (Old Regulations): J. R. Brooke, Pharmaceutical Society's Laboratories and King's Coll., London; M. Priest, Finsbury Tech. Coll.; and T. Tickle, Pharmaceutical Society's Laboratories, King's Coll. and Univ. Coll. London. *Final A.I.C. Examination* (Branch "A," Mineral Chemistry): W. A. Fyffe, Univ. Coll., Dundee; and L. V. Wright, B.A., Sidney Coll., Cambridge. *Branch "B" (Metalurgical Chemistry)*: H. J. Winch, A.C.G.I., City and Guilds of London Central Institution and Finsbury Tech. Coll. *Branch "C" (Physical Chemistry)*: T. S. Price, B.Sc. (Lond.), Ph.D. (Leipzig), Mason Univ. Coll., Birmingham, and the Universities of Leipzig and Stockholm. *Branch "D" (Organic Chemistry)*: F. G. Edmed,

Assoc.R.C.Sc. (Lond.), B.Sc. (Lond.), Royal College of Science, London; L. Eynon, Finsbury Tech. Coll.; H. Hall, Univ. Coll., Nottingham, and F. Shedden, B.Sc. (Lond.), Mason Univ. Coll., Birmingham. *Branch "E" (the Analysis of Food and Drugs, including an Examination in Therapeutics, Pharmacology, and Microscopy)*: L. W. Stansell, Maidstone, and W. Thorp, B.Sc. (Lond.), Limerick, both for the Fellowship. The Examiners in Chemistry were Dr. Bernard Dyer, D.Sc. (Lond.), F.I.C., and Professor Percy F. Frankland, F.R.S., F.I.C., and the Examiner in Therapeutics, Pharmacology, and Microscopy was Dr. Thomas Stevenson, M.D., F.R.C.P.

NOTES AND QUERIES.

Water Analyses.—I have had a sample of water submitted to me for analysis, and have obtained the following results, in parts per 100,000:—

Total solids	62.0
Sulphate of lime	40.2
Chlorine	2.4
Free ammonia	0.001
Albumenoid ammonia	0.0034
Poisonous metals	nil

Can any reader inform me if this water may be pronounced fit for drinking purposes, or is the sulphate of lime excessive? The books and journals which I have access to do not help me to decide the matter. Information on the subject will be gratefully received.—N. H.

MEETINGS FOR THE WEEK.

- MONDAY, 29th.**—Society of Arts, 8. (Cantor Lectures). "The Nature and Yield of Metalliferous Deposits," by Bennett H. Brough.
- TUESDAY, 30th.**—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester M.A., LL.D., F.R.S.
- Society of Arts, 8. "Niello Work," by Cyril Davenport.
- WEDNESDAY, 31st.**—Society of Arts, 8. "The Undeveloped Resources of the Bolivian Andes," by Sir Martin Conway, M.A.
- THURSDAY, Feb 1st.**—Royal Institution, 3. "The Senses of Primitive Man," by W. H. R. Rivers, M.A., M.D.
- Chemical, 8. "The Chlorine Derivatives of Pyridine—Part V. Synthesis of $\alpha\alpha$ -Dichloropyridine and Constitution of Citrazinic Acid," by W. J. Sell, M.A., and F. W. Dootson, M.A. "The Formation of Heterocyclic Compounds," by S. Rahemann and H. E. Stapleton. "The Space Configuration of Quadrivalent Sulphur Derivatives—Methylethylthetin-dextrocamphorsulphonate and Dextrobromocamphorsulphonate," by W. J. Pope and S. J. Peachey. "Nitrocamphane," by M. O. Forster.
- FRIDAY, 2nd.**—Royal Institution, 9. "Wireless Telegraphy," by G. Marconi, M.Inst.E.E.
- SATURDAY, 3rd.**—Royal Institution, 3. "Neglected Byways in Music" (with Musical Illustrations), by Sir Hubert H. Parry, Mus. Doc., M.A., D.C.L.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2097.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART II.

By HARRY BREARLEY.

(Continued from vol. lxxx., p. 273).

TUNGSTEN AND MOLYBDENUM.

THIS section is compiled from the following journals:—

CHEMICAL NEWS, 1860 to 1899, vols. i. to lxxx.

Journal of the Iron and Steel Institute, 1880 to 1899.

Journal of the Chemical Society, 1885 to 1898, vols. xlvii. to lxxiv.

Journal of the Society of Chemical Industry, 1882 to 1898, vols. i. to xvii.

The general arrangement for both elements alike is—

I. SEPARATION FROM OTHER ELEMENTS.

II. GRAVIMETRIC ESTIMATIONS.

III. VOLUMETRIC ESTIMATIONS.

IV. DETECTION AND MISCELLANEOUS NOTES.

The analytical characters of the two metals are so similar that the means of separating or estimating the one frequently apply to the other also. Attention is drawn to such facts when they occur, but they are not separately mentioned under each element.

Tungsten having come into general use within the last dozen years or so, and molybdenum being hardly in general use even now, the analysis of steel works compounds of these metals has no very extensive literature. On this account, references to the analysis of compounds foreign to steel works practice are included in order that the processes for the one may, perhaps, be adapted to the other material.

Special attention is drawn to the fact that SiO_2 and WO_3 cannot be separated by ammonia. Dufty, in a paper read before the Sheffield Metallurgical Society, seems first to have drawn attention to this fact, but Skey and Pibram had previously (219) observed the solubility of even ignited silica in ammonia.

Some references, chiefly to volumetric processes of estimating molybdenum, are properly associated with the molybdate process of estimating phosphorus.

TUNGSTEN.

I. SEPARATION FROM OTHER ELEMENTS.

218. *Iron*.—BENNEVILLE (*J. I. S. I.*, 1895, i., 205).—Fuse with Na_2CO_3 , KNO_3 , and NaHO ; extract with water, and evaporate with HCl . Fe and Mo are also separated by fusion. (See 258 and 259).

219. *Silicon*.—SKEY (*C. N.*, xvii., 165).—Hydrous SiO_2 is sensibly dissolved in ammonia, and is partly soluble even after strong ignition. PIBRAM (*C. N.*, xvii., 227) determines the solubility of variously treated silica in ammonia.

o VIGOUROUX (*C. N.*, lxxviii., 291).—Silicide of tungsten is analysed by heating with chlorine. The silicon chloride is volatilised and finally weighed as SiO_2 .

221. WADDELL (*C. N.*, l., 113).—By fusion with KHSO_4 , &c.; also with ammonia.

222. BENNEVILLE (*J. S. C. I.*, 1897, 636).—Several evaporations with HF are sometimes necessary to remove all the SiO_2 from WO_3 . Accurate separation with ammonia not possible.

223. *Tin*.—RAMMELSBERG (*C. N.*, ix., 25).—Rose's process consists in reducing the metals in hydrogen, and dissolving out the tin with HCl (see 274). It is difficult to reduce the WO_3 , and the tin may volatilise. By igniting with $(\text{NH}_4)\text{Cl}$ stannic acid is vapourised; WO_3 remains. Repeat process to constant weight (see 279).

224. TALBOTT (*C. N.*, xxii., 190).—Fuse oxides with KCN. The tin is reduced to metal and filtered from alkaline tungstate dissolved in water. Mo is not similarly separated.

225. DONATH and MÜLLNER (*J. C. S.*, liv., 531).—Oxides mixed with zinc dust, ignited, boiled with HCl , oxidised with KClO_3 , and WO_3 filtered off.

226. *Phosphorus*.—KEHRMANN (*J. I. S. I.*, 1887, ii., 371).—Boil acids with NaHO ; $(\text{NH}_4)\text{Cl}$ and $(\text{NH}_4)\text{HO}$ added, and the P precipitated with magnesia mixture. Filtrate must be evaporated four times to recover the WO_3 .

227. *Vanadium*.—FRIEDHEIM (*C. N.*, lxi., 220).—The acids are precipitated together with HgNO_3 and HgO , and moist precipitate dissolved in HCl ; on largely diluting, the WO_3 is re-precipitated and separated by filtration.

228. GIBBS (*J. C. S.*, xlvii., 713).—Slightly alkaline solution boiled with large quantity of $(\text{NH}_4)\text{NO}_3$; metavanadate precipitated on standing. ROSENHEIM (*J. C. S.*, lvi., 762) says Gibbs's process is erroneous.

229. ROTHENBACH (*J. C. S.*, lx., 18).—The acids precipitated together with HgNO_3 ; the vanadic acid determined separately by reduction and titration with KMnO_4 , or by boiling with H_3PO_4 , KBr , and HCl , absorbing liberated Br in KI, and titrating the free iodine.

230. BROWNING and GOODMAN (*J. C. S.*, lxxii., 234).—Va can be estimated in the presence of both W and Mo by reducing with some organic acid, and titrating with iodine (see also 281).

231. *Titanium*.—DEFACQZ (*C. N.*, lxxiv., 293).—Heated with KNO_3 and K_2CO_3 ; W in water extract; precipitate as mercurous tungstate.

232. *Gold*.—SMITH and WALLACE (*J. C. S.*, lxii., 920).—Both W and Mo are separated electrolytically.

233. *Molybdenum*.—FRIEDHEIM and MEYER (*J. C. S.*, lxiv., 125).—Tungsten compounds always contain molybdenum; it is separated as sulphide from a solution of the metatungstate.

234. BENNEVILLE (*J. I. S. I.*, 1895, i., 209).—Precipitated together as lead salts, heated in stream of HCl , residual tungsten determined, and Mo calculated by difference.

235. SMITH and OBERHOLTZER (*C. N.*, lxviii., 6).—By volatilising Mo in current of HCl . SMITH and MAAS (*C. N.*, lxviii., 207) make an atomic weight determination in this way.

236. WADDELL (*C. N.*, lv., 101).—Add tartaric acid to prevent precipitation of WO_3 on acidification; the Mo is then precipitated with H_2S .

237. DESI (*J. C. S.*, lxxiv., ii., 231).— WO_3 insoluble in H_2SO_4 ; MoO_3 easily dissolved; hence a means of separating them (see also 287).

238. *Antimony*.—HALLOPEAU (*J. C. S.*, lxxiv., ii., 540).—The metals are precipitated as mercurous antimonio-tungstate, ignited to oxides, and the antimony reduced by fusion with KCN.

239. *Antimony, Arsenic, and Iron*.—COBENZL (*C. N.*, xlvii., 13).—Digest with aqua regia, evaporate, take up with HNO_3 and tartaric acid, and filter off WO_3 (see 280).

240. *Silver, Mercury, and Cadmium*.—SMITH and FRANKEL (*J. S. C. I.*, 1890, 1067).—Separated electrolytically from both W and Mo.

240a. *Chromium*.—SMITH and DIECK (*C. N.*, lxviii., 68).—Evaporate with HCl . Pure WO_3 remains insoluble on again digesting with HCl . (See 263).

240b. *Various*.—IBBOTSON and BREARLEY (C. N., lxxx., 293).—The alkalis, alkaline earths, Zn, Cd, Mn, Ni, Co, Hg, As, Ur, and Fe do not interfere with the precipitation of W as $PbWO_4$ followed by solution in HCl, and precipitation of WO_3 by diluting.

(To be continued).

A CONTRIBUTION TO THE STUDY OF LIQUID MIXTURES OF CONSTANT BOILING-POINT.*

By GARNETT RYLAND.

(Concluded from p. 43).

General Investigation of the Boiling-points of Binary Mixtures of Liquids Mutually Soluble in all Proportions.

ALL liquids boiling below 170° that were at hand were purified; and each was mixed with every other whose boiling-point was within $30-40^\circ$ of its own, and the mixture distilled. When a constant boiling mixture was found, the ratio of its constituents was determined as nearly as possible by repeated mixing in various proportions, and careful distillation until that ratio was discovered for which the whole mixture distilled most nearly within 1° . A volume of 10–15 c.c. was found adequate for each trial mixture distilled.

The ratio of the products of the respective vapour-densities and vapour-tensions at a temperature near that of constant boiling was calculated whenever the necessary data were known, and is given below as the "theoretical ratio."

1. Methyl alcohol ($64.5-65^\circ$) and ethyl bromide ($37.5-38.5^\circ$) are distilled at $35-36^\circ$ (765 m.m.) in the approximate ratio of 5:95 parts by weight. Theoretical ratio at 35° , 9:91 parts by weight.

2. Methyl alcohol and chloroform ($60-61^\circ$) at $53.5-54.5^\circ$ (765 m.m.); ratio, 12:88. Theoretical ratio at 55° , 17:83.

3. Methyl alcohol and methyl acetate ($55.5-56.5^\circ$) at $53.5-54.5^\circ$ (760 m.m.); ratio, 18:82.

4. Methyl alcohol and ethyl iodide (see Wanklyn p. 16, *ante*) ($72.3-72.5^\circ$) at $54.5-55.5^\circ$ (770 m.m.); ratio, 17:83. Theoretical ratio at 55° , 19:81.

5. Methyl alcohol and ethyl acetate ($75.5-76.5^\circ$) at $61.7-62.5^\circ$ (757 m.m.); ratio, 47:53.

6. Methyl alcohol and benzene. (See p. 42, *ante*).

7. Methyl alcohol and isobutyl iodide ($118-119^\circ$) at $63.5-64.5^\circ$ (760 m.m.). The ratio of 70:30 parts by weight gave an excess of alcohol. In this and all succeeding distillations of isobutyl iodide mixtures, the formation of tar made a close determination of the proportions impossible.

Methyl alcohol is separated by fractional distillation from ether ($34.5-35.5^\circ$), acetone ($56-57^\circ$), and toluene ($108.5-109.3^\circ$).

8. Ethyl alcohol ($77.5-78^\circ$) and ethyl bromide $37.5-38.5^\circ$ at $36.5-37.5^\circ$ (762 m.m.). The theoretical ratio at 37.5° is 6.6:93.4. The actual per cent of alcohol seemed to be about half of the theoretical, but could not be more closely determined.

9. Ethyl alcohol and carbon disulphide (see Berthelot, p. 16, *ante*) ($45.5-46^\circ$) at $41.5-42.5^\circ$ (755 m.m.); ratio, 9:91, verified. Theoretical ratio at $43-44^\circ$, 11.4:88.6.

10. Ethyl alcohol and chloroform ($60-61^\circ$) at $58.5-59.5^\circ$ (759 m.m.); ratio, 6:94. Theoretical ratio at 60° , 15.6:84.4.

11. Ethyl alcohol and ethyl iodide ($71.5-72.5^\circ$) at $62.5-63.5^\circ$ (761 m.m.); ratio, 14:86. Theoretical ratio at 60° , 17.4:82.6.

12. Ethyl alcohol and ethyl acetate ($75.5-76.5^\circ$) at $71-72^\circ$ (765 m.m.); ratio, 31:69.

13. Ethyl alcohol and benzene. (See p. 42, *ante*).

14. Ethyl alcohol and isobutyl iodide ($118-119^\circ$) at $76.5-77.5^\circ$ (760 m.m.); approximate ratio, 70:30.

Ethyl alcohol is separated from propyl alcohol (97.5°) and toluene ($108.7-109.3^\circ$).

15. Isopropyl alcohol ($81-82^\circ$) and carbon disulphide $45.5-46^\circ$ at $43.5-44.5^\circ$ (761 m.m.); ratio, 9:91.

16. Isopropyl alcohol and ethyl iodide ($71.5-72.5^\circ$) at $65.5-66.5^\circ$ (764 m.m.); ratio, 13:87.

17. Isopropyl alcohol and ethyl acetate ($75.5-76.5^\circ$) at $74-75^\circ$ (770 m.m.); approximate ratio, 26:74.

18. Isopropyl alcohol and benzene ($79-79.5^\circ$) at $71-72^\circ$ (758 m.m.); ratio, 30:70.

19. Isopropyl alcohol and water at $78.5-79.5^\circ$ (768 m.m.); ratio, 89:11.

(See Linnemann, p. 16, *ante*). The per cent of water in the compounds $3C_3H_8O.2H_2O$, $2C_3H_8O.H_2O$, and $3C_3H_8O.H_2O$ is 16.7, 13, and 9 per cent respectively. The alcohol used by me was distilled from lime at $81-82^\circ$. This case should be investigated further).

20. Isopropyl alcohol and isobutyl iodide ($118-119^\circ$) at $81-82^\circ$ (761 m.m.); approximate ratio, 70:30.

Isopropyl alcohol is separated from chloroform ($60-61^\circ$) and toluene ($108.7-109.3^\circ$).

21. Normal propyl alcohol (95.7°) and ethyl iodide ($72.3-72.5^\circ$) at $69.5-70.5^\circ$ (768 m.m.); approximate ratio, 7:93.

22. Propyl alcohol and benzene ($79-79.5^\circ$) at $76-77^\circ$ (762 m.m.); ratio, 16.5:83.5. Theoretical ratio at 80° , 28.5:71.5.

23. Propyl alcohol and water at $87-87.5^\circ$ (770 m.m.); ratio, 72:28.* Theoretical ratio at 87.5° , 79:21.

24. Propyl alcohol and toluene ($108.7-109.3^\circ$) at $91-92^\circ$ (765 m.m.); ratio, 53:47.

25. Propyl alcohol and isobutyl iodide ($118-119^\circ$) at $92.5-93.5^\circ$ (753 m.m.); approximate ratio, 45:55.

Normal propyl alcohol is separated from ethyl acetate ($75.5-76.5^\circ$) and isobutyl alcohol ($105.3-106.3^\circ$).

26. Isobutyl alcohol ($105.3-106.3^\circ$) and toluene $108.8-109.3^\circ$ at 100° (764 m.m.); ratio, 43:57.

27. Isobutyl alcohol and isobutyl iodide ($118-119^\circ$) at $101-102^\circ$ (765 m.m.). The ratio of 33:67 gave an excess of alcohol.

28. Isobutyl alcohol and ethylene bromide ($129-130^\circ$) at $104.5-105.5^\circ$ (763 m.m.); approximate ratio, 62:38.

Isobutyl alcohol is separated from ethyl iodide ($72.3-72.5^\circ$), benzene ($78.5-79^\circ$), and metaxylene ($136-137^\circ$).

29. Amyl alcohol ($128-129^\circ$)† and isobutyl iodide ($118-119^\circ$) at $115-116^\circ$ (765 m.m.). The ratio of 20:80 gave a slight excess of iodide.

30. Amyl alcohol and ethylene bromide ($129-130^\circ$) at $121-122^\circ$ (760 m.m.); ratio, 30:70. Ratio of vapour-densities, 32:68.

31. Amyl alcohol and metaxylene ($136-137^\circ$) at $125-126^\circ$ (760 m.m.); ratio, 52:48. Amyl alcohol and paraxylene ($137-137.5^\circ$) at $125-126^\circ$, in the same ratio; and amyl alcohol and orthoxylene ($140-141^\circ$) at $127-128^\circ$, with a slightly larger per cent of alcohol.

Amyl alcohol is separated from toluene ($108.8-109.3^\circ$).

32. Amyl alcohol ($95-96^\circ$) and benzene ($79-79.5^\circ$) at $76-77^\circ$ (760 m.m.). The ratio of 20:80 gave a slight excess of alcohol.

33. Amyl alcohol and toluene ($108.8-109.3^\circ$) at $91-92^\circ$ (756 m.m.); approximate ratio 50:50.

34. Acetic acid ($117-118^\circ$) and toluene ($108.8-109.3^\circ$) at $103.5-104.5^\circ$ (761 m.m.); ratio, 30:70.

35. Acetic acid and metaxylene ($136-137^\circ$) at $113.5-114.5^\circ$ (761 m.m.); ratio, 27:73.

Acetic acid is separated from carbon disulphide ($45.5-45.7^\circ$) and benzene ($79-79.5^\circ$).

36. Butyric acid ($159-160^\circ$) and water at $99-99.5^\circ$

* See Konowalow, and Ramsay and Young, p. 16 (*ante*). My determination of the ratio was made before I knew of that found by Ramsay and Young.

† This was obtained by repeated fractionation from the commercial mixture of amyl alcohols.

* From the *American Chemical Journal*, vol. xxii., No. 5, Nov., 1899.

(763 m.m.); ratio, 20:80 (see Konowalow, p. 16, *ante*). Theoretical ratio at 100°, 32:68.

37. Butyric acid and brombenzene (152—153°) at 147—148° (748 m.m.); ratio, 19:81.

38. Ether (34°5—35°5') and carbon disulphide (45°5—46°) at 34°5—35°5' (768 m.m.); approximate ratio, 65:35. Theoretical ratio at 35°, 59:41.

Ether is separated from acetone (56—57°) and chloroform (60—61°). A mixture of ether and ethyl bromide (37°5—38°5') is distilled at the same temperature (35—38°) as its constituents.

39. Carbon disulphide (45°5—45°7') and ethyl bromide (37°5—38°5') at 37—38° (770 m.m.); ratio, 32:68. Theoretical ratio at 37°5', 35:65.

40. Carbon disulphide and acetone (55°5—56°5') at 38°5—39°5' (766 m.m.); ratio, 74:26. Theoretical ratio at 40°, 66:34.

41. Carbon disulphide and methyl acetate (55°5—56°5') at 39—40° (756 m.m.); ratio, 71:29.

42. Carbon disulphide and ethyl acetate (75°5—76°5') at 45°5—46°5' (768 m.m.); ratio, 92:8.

Carbon disulphide is separated from chloroform (60—61°), ethyl iodide (71°5—72°5'), and benzene (79—79°5').

43. Acetone (55°5—56°5') and methyl acetate (55°5—56°5') in about equal parts are distilled 0°5' below the boiling-point of ether.

44. Acetone and ethyl iodide (71°5—72°5') at 55—56° (770 m.m.); approximate ratio, 60:40.

45. Acetone and chloroform (60—61°) at 64—65° (760 m.m.); approximate ratio, 20:80.

Acetone is separated from ethyl bromide (37°5—38°5') and ethyl acetate (75°5—76°5').

46. Chloroform (60—61°), and methyl acetate (55°5—56°5') at 64—65° (760 m.m.); approximate ratio, 78:22.

Chloroform is separated from ethyl bromide (37°5—38°5'), ethyl iodide (71°5—72°5'), ethyl acetate (76—77°), and benzene (79—79°5').

47. Ethyl iodide (71°5—72°5'), and ethyl acetate (75°5—76°5'), at 69°5—70°5' (762 m.m.); approximate ratio, 78:22.

48. Ethyl iodide and benzene (79—79°5') at 74—75° (758 m.m.); approximate ratio, 80:20.

Ethyl acetate (75°5—76°5') is separated from benzene (79—79°5').

Isobutyl iodide (118—119°) is separated from toluene (108°7—109°3').

Acetone (55°5—56°5'), and benzene (79—79°5') in the ratio of 5:1 approximately, showed a tendency to gather at 57—58°, this fraction constantly increasing throughout the course of repeated distillations. But the proportions could not be found for which all of the mixture would boil at this point, as in every case there were small fractions from 57° to 79°.

Ethylene bromide (129—130°) and metaxylene (136—137°), in the ratio of 5:2 approximately, showed a similar tendency to gather at 130—131°.

Amyl alcohol (128—129°), and brombenzene (152—153°), in the ratio of 5:2 approximately, seemed to be distilled at 128—129°, but the small per cent of the latter and the formation of tar prevented a definite determination.

Summary.—Of the 80 mixtures examined, 45 were distilled at a constant temperature at or below the boiling-point of the more volatile constituent; 2 (Nos. 45 and 46), at a constant temperature above the boiling-point of the less volatile constituent; 1 (Nos. 48), at a constant temperature between the boiling-points of the constituents; 1 (ether-ethyl bromide), in which the boiling-points of the constituents are too close for fractionation, presents no relative depression or elevation of the boiling-point of the mixture; and 3 are of an uncertain character.

Boiling points of Mixtures of Liquids whose Mutual Solubilities are Limited.

Two cases of this kind were examined.

1. Isobutyl alcohol (105°3—106°3'), saturated with water at the temperature of the room (about 5 parts of alcohol to one part of water) boils for a time at the con-

stant temperature of 89—90°, the distillate separating in the receiver into two layers. The excess of alcohol above the amount necessary for the proportions of distillation at constant temperature causes the temperature to rise gradually to 106°. If the alcohol is saturated at higher temperatures, the portion distilling at 89—90° is correspondingly larger.

2. Methyl alcohol (64°5—65°), saturated with carbon disulphide (45°5—46°) (about equal parts by weight at the temperature of the room), boils for a time at 37—38°. The excess of alcohol causes the temperature to rise ultimately to 65°. This mixture shows phenomena similar to those noted in case 1.

Conclusions.

1. The large proportion of constant boiling mixtures found in the cases examined makes it evident that this phenomenon is by no means so exceptional as has hitherto been supposed. In fractional distillation one should always be on his guard against it.

2. The changes in the composition of the distillates, corresponding to the changes in pressure and temperature of the distillation, indicate that the two mixtures investigated (see p. 42, *ante*), are not true chemical compounds, and that any approximation to molecular proportions must be regarded as accidental.

3. It is well known that two liquids mutually insoluble are distilled at a constant temperature in the ratio of the products of their respective vapour-densities and vapour-tensions at the temperature of distillation.

If the liquids are partially soluble in each other, they are also distilled at a constant temperature, but with some deviation from this ratio, so long as there are two layers of liquids in the distilling flask.

The results of this investigation are generally in accord with the theory that when two liquids, mutually soluble in all proportions, are distilled at a constant temperature, their ratio in the distillate is that of the products of the vapour-densities and vapour-tensions of the pure liquids at that temperature, modified more or less by their influence upon each other.*

ON GADOLINIUM.†

By C. BENEDICKS.

Introduction.

THE study of the so-called rare-earths was pursued in a new direction in the year 1873, on the appearance of Cleve and Höglund's work on the salts of yttrium and erbium. Hitherto the experimenters whose names are connected with the history of the rare earths had specially devoted their attention to the pure production of a certain oxide, in order to determine its atomic weight, the phenomena exhibited by its spectrum, and the common properties of the salts. The first result of such experiments was the establishment of the tri-atomicity of these elements. It is clear that in this direction we may expect other important results for this interesting, but obscure, field of chemical research, at least so soon as similar material is acquired from a larger number of more closely examined earths. With reference to this, Prof. Dr. P. T. Cleve has requested me to work upon the salts of gadolinium. In the following I shall report upon this work, and shall also mention what is so far known concerning this element.

I take this opportunity of acknowledging my gratitude to Prof. Dr. P. T. Cleve for the interest and advice he has accorded me during the work.

* The greatest deviation from the calculated ratio was found in the mixture of propyl alcohol and benzene (No. 22).

† *Zeitschrift für Anorganische Chemie*, xxii., 5, p. 393.

Historical.

In the year 1880, Marignac discovered a new earth in samarskite—a mineral which, two years before, had been found in great quantity in North Carolina. He succeeded in isolating two different oxides which were formerly called by him $Y\alpha$ and $Y\beta$. $Y\beta$, which was identified by the yellow colour and the absorption spectrum of its salts, was later found to be identical with the oxide of samarium, discovered by Lecoq de Boisbaudran in 1879.

Marignac, with his well-known accuracy, ascribed to the earth $Y\alpha$, which had no absorption spectrum, and whose salt solutions were colourless, properties which at once characterise it as the oxide of a new element. I quote the following extract from his work:—"The existence of this base as a separate earth is made evident by the fact that its equivalent is a maximum between those which come next to it by their solubility in potassium sulphate." . . . "It should not be confounded with any one of those so far identified."

The solubility in saturated potassium sulphate solution, which divides $Y\alpha$, on the one hand, from easily soluble ytterbium and terbium oxides, and, on the other hand, from difficultly soluble samarium oxide ($Y\beta$), was stated by Marignac to be such that 1 grm. oxide was held in solution as double sulphate of potassium by 100—150 c.c. potassium sulphate solution; and this statement was later fully corroborated (by Bettendorff and me). The atomic weight was found by Marignac to be 156.75 (equivalent

weight $RO = 120.5$), which agrees pretty closely with the later found values.

But, according to Marignac, it was possibly that his earth $Y\alpha$ was identical with philippium, found shortly before by Delafontaine. Added to this, mosandrium, identified by Law. Smith, was still doubtful, though looked upon by Marignac and Delafontaine as terbium, and he hesitated for the present to give his earth a name. He writes:—"I do not consider it yet necessary to give a name to this new earth. It will be time enough when one is certain of having obtained it in a state of purity, and succeeded in preparing its salts in sufficient quantity for examination."

Afterwards, Marignac's work was continued by Lecoq de Boisbaudran, by successive fractionation with dilute ammonia. The atomic weight determinations carried out by him, and which agreed well with those of Marignac, have placed the individuality of $Y\alpha$ beyond doubt. After he had proved mosandrium to be a mixture of $Y\alpha$ and terbium, he, with the concurrence of Marignac, fixed for $Y\alpha$ in 1886 the name gadolinium, with the symbol Gd.

It is certainly very questionable if this name is appropriate for a fundamental substance, in conformity with the usual practice in chemistry not to derive names of so much importance as those of the fundamental substances from persons, however eminent. The name is derived from the Finnish chemist Gadolin, who, in 1794, discovered the mineral gadolinite, afterwards named after him.

However, the same remark might be made with reference to the name samarium (the mineral samarskite is called after the Russian v. Samarski), and as the name gadolinium is already enrolled in literature, it might not be advisable to replace it by another.

In the year 1892 Bettendorff produced a pure specimen of gadolinium earth. He carried out atomic weight determinations in various potassium sulphate fractions, from which it appeared that in these there was no variation of the atomic weight. Also, by partial precipitation with ammonia, an earth with a quite unaltered atomic weight was obtained, and by this Bettendorff established the identity of gadolinium.

A new method of fractionating was proposed in 1896, when Demarçay crystallised a mixture of gadolinium and samarium nitrates in concentrated nitric acid, and expected to find in the fraction between gadolinium (which crystallises first) and samarium (which remains more in

the mother-liquor) a new element, distinguishable by its spark spectrum from the above-mentioned and remaining earth elements. In the following I will give a fuller description of this.

Methods of Separation and Material.

For the isolation of gadolinium from accompanying earths, Marignac made use of the difference in solubility in potassium sulphate solution, by which gadolinium is distinguished from the more soluble yttrium and terbium, and the less soluble samarium (and didymium); this method is tedious from much repetition. It must be combined with partial precipitation by ammonia, in order to obtain a pure product, especially in the case of separating terbium. By this means, terbium and samarium are precipitated before gadolinium, and didymium after gadolinium. The material kindly placed at my disposal by Professor Cleve included various minerals, and was in part already worked out by him. Results showed that Demarçay's crystallisation process with concentrated nitric acid is very well adapted to the separation of gadolinium in the case of a mixture of gadolinium and samarium. In order to discover how a mixture of gadolinium and yttrium would behave under similar circumstances, I made three crystallisations of such a mixture with atomic weight $R = 143.4$; the concentrated nitric acid used having the specific gravity 1.54.

The atomic weight of the earth in the first mother-liquor was determined, as also that of the crystals from the third mother-liquor, and the following values found:—

$$\begin{array}{c} R = 143.4 \\ \swarrow \quad \searrow \\ 1 \quad 2 \quad 3 \quad 4 \\ R = 127.1 \quad R = 151.1 \end{array}$$

In the above scheme, 1, 2, 3 are the first, second, and third mother-liquors, and 4 the crystals from 3. From this result it is evident that the nitric acid crystallisation is a specially active means of separating gadolinium also from yttrium.

I have convinced myself by special tests that the nitrates of triatomic cerium, praseodymium, neodymium, and lanthanum do not crystallise, or only with difficulty, in concentrated nitric acid; hence gadolinium nitrate is less soluble in concentrated nitric acid than the nitrates of the remaining earths.

In one material, which was obtained as the first ammonia precipitates of a gadolinium-yttrium mixture, a holmium (or dysprosium) line was still visible after about fifteen re-crystallisations: this indicates that the nitrate of the element in question is difficultly soluble, as is that of gadolinium.

Successful separation of gadolinium from terbium was not attained by this means, for the gadolinium oxide obtained after several re-crystallisations is only slightly lighter in colour than the original material. I also carried out a fractionating experiment with the chlorides in concentrated hydrochloric acid, but with a much less satisfactory result, viz., with the same material as before the result thus obtained was—

$$\begin{array}{c} R = 143.4 \\ \swarrow \quad \searrow \\ 1 \quad 2 \quad 3 \quad 4 \\ R = 139.3 \quad R = 146.6 \end{array}$$

The quickest method for obtaining pure gadolinium seems to me to be that which I used later, viz., to fractionate the nitrate in concentrated nitric acid after the weaker bases have been removed, and then partial precipitation with cold dilute ammonia. (The ammonia should always be used dilute, so that precipitation takes place slowly). By this means the terbium and samarium earths are obtained in the first precipitates; in the last, a faintly coloured and finally almost pure white gadolinium oxide is obtained. The traces of didymium which were still present at the crystallisation of the nitrates are best re-

moved by a new series of crystallisations of the nitrates. The advantage of the crystallisation process is obvious, for by this means a greater number of operations can be carried out in the same time as a single tedious potassium-sulphate precipitation.

The concentrated nitric acid forms fairly easily super-saturated solutions of the nitrates, wherefore it is advantageous to add a few crystals to the solution.

During the progress of my work a quantity of nearly pure gadolinium earth was added to the material I had purified, by the kindness of Prof. Cleve.

Atomic Weight of Gadolinium.

As already mentioned, Marignac found for the equivalent weight of $\text{Y}_2\text{RO} = 120.5$, which indicated an atomic weight of $\text{R} = 156.75$ for gadolinium. Lecoq de Boisbaudran obtained from Marignac's original material, after further purification, the number 155.95, or, after allowing for the probable effect of impurities, 156.15. Cleve found 155 with his earth, in which Lecoq found later some samarium to be present, which had somewhat lowered the atomic weight. Bettendorff, whose determinations may be of greater value than the former, having been carried out with purer material, obtained as a mean result the number 156.33. It seems to me to have been proved that the atomic weight of gadolinium cannot be far from the number 156.

My own determinations, carried out in the usual way, by converting a weighed quantity of oxide into sulphate, give 156.38 as a mean result. But the fractional part of this value seems uncertain, and in the following I shall use the round number 156 to simplify matters. My object is to undertake a determination of the atomic weight later.

The remaining atomic weights used in my work are those of the Commission of the German Chemical Society, 1898.

(To be continued).

SEPARATION OF COPPER FROM CADMIUM.

By G. BORNEMANN.

COPPER is precipitated quantitatively from its neutral boiling solutions by oxalic acid, even if we add four times the theoretical quantity of this reagent necessary; but the precipitate does not deposit well, and is difficult to wash, as it passes through the pores of the filter-paper. If the solution is made slightly acid with nitric acid we can get a much more rapid deposition of the precipitate, and the filtration is made much easier; but in this case, care must be taken not to use a large excess of oxalic acid, and a special paper must be used for filtration; the precipitate must be washed with water containing a little oxalic acid. The analysis of the oxalate of copper, dried at 110° till the weight is constant, leads to the formula $6\text{CuC}_2\text{O}_4 + \text{H}_2\text{O}$.

As for the separation of copper and cadmium by means of oxalic acid, it has been found that this separation is only possible in boiling nitric solution, otherwise a part of the cadmium is precipitated in the state of oxalate. Further, a small quantity of this salt separates if the nitric solution is cooled. The quantity of oxalic acid used should not exceed the quantity theoretically equivalent to the sum of the copper and cadmium present in the solution. On the other hand, a quantity of nitric acid equal to the quantity of oxalic acid may be added. The presence of ammoniacal compounds does not interfere with the precipitation.

The method of working is as follows:—

The moderately concentrated solution is made slightly acid with nitric acid, and then heated to boiling point and a boiling solution of oxalic acid (saturated in the cold) added, in quantity slightly greater than that of the copper

present. The mixture is placed on a boiling water-bath, and left to stand until the supernatant liquid is perfectly clear. The liquid is then carefully decanted on to a filter, after the addition of a little nitric and oxalic acids, and the precipitate washed with acidulated water, and finally with boiling distilled water.

The precipitate of oxalate of copper is dried, detached as much as possible from the filter-paper, and placed in a Rose's crucible. The filter paper is burnt and the ash added to the bulk of the precipitate, a little sulphur is added, and the whole calcined in a current of hydrogen. Finally, the cuprous sulphate is weighed.

If the precipitated oxalate contains cadmium, a yellow stain of sulphide of cadmium will be observed on the crucible and on the surface of the cuprous sulphide.

The cadmium is determined in the filtrate in the usual manner.

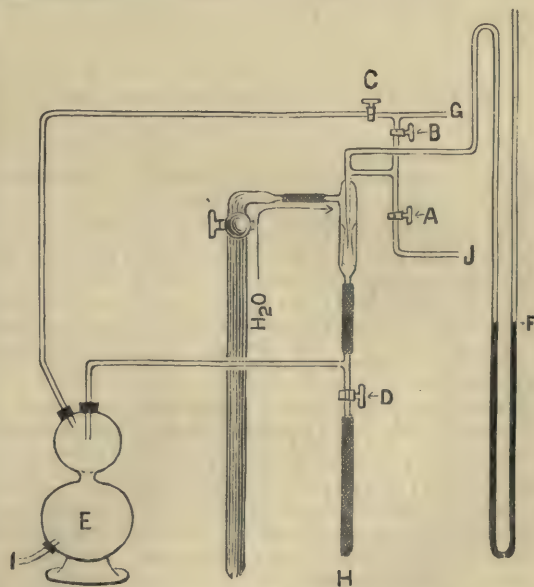
The author prepared a solution containing 6.200 grms. of CuO , and 9.885 grms. of CdO per 100 c.c.. On proceeding as above described he found an average of 6.210 grms. of CuO , and 9.872 grms. of CdO .—*Chemiker Zeitung*, 1899, xxii. [53], p. 565.

A COMBINED EXHAUSTER AND BLOWER.

By EDWIN DOWZARD, F.C.S.

In the majority of chemical laboratories connected with manufacturing concerns, the supply of apparatus is not prodigal, and a chemist has frequently to utilise old and damaged pieces of apparatus.

In the accompanying illustration it is shown how, with the aid of a damaged Kipp's H_2S apparatus, an ordinary filter-pump may be converted into a combined exhauster and blower.



We will suppose that the water is turned on, and the taps A, B, C and D are open. If D and B are closed, the mixture of water and air from the pump will pass into the Kipp's apparatus, instead of passing through H; in a few seconds the outlet I will be covered, and a current of air will be delivered at G; of course the taps A and C must be left open. It is necessary to regulate the size of the outlet I, so that the water in E never reaches higher than the dotted line.

If we now open D and B and close C, there will be suction at G and J; the vacuum so produced (if used to

exhaust distillatory apparatus, &c.) is measured by the gauge F.

Of course the taps A, B, C, and D may be replaced by burette clips, &c.

THE VOLUMETRIC ESTIMATION OF SULPHUR IN CAST-IRON, STEEL, &c.

By J. THILL.

By attacking the metal with hydrochloric acid in the well-known apparatus used for this purpose, the sulphur is liberated as sulphuretted hydrogen. The gas is received in 25 c.c. of a decinormal solution of arsenious acid, to which has been added 50 c.c. of a cold saturated solution of bicarbonate of soda. Care should be taken that the gas is not given off too rapidly.

When the attack is finished, the gas which still fills the apparatus is driven out by means of a current of carbonic acid, and the passage of this current of gas is continued until the hydrochloric acid carried with it has neutralised the alkaline solution, and precipitated almost the whole of the trisulphide of arsenic. This operation takes eight or ten minutes.

We then add a few c.c. of hydrochloric acid, make up the volume to 500 c.c., and filter. The filtrate is collected in a dry beaker, and 100 c.c. are taken, and titrated with N/50 iodine, after adding starch and a sufficient quantity of carbonate of ammonia to render the solution alkaline.

From the number of c.c. of iodine used, we subtract the number of c.c. required by 25 c.c. of a decinormal solution of arsenious acid. The difference corresponds to the sulphuretted hydrogen given off. This result multiplied by 0.0024045, gives the amount of sulphur contained in the sample.—*Zeits. Anal. Chem.*, xxxviii., p. 342.

ELECTROLYTIC ESTIMATION OF ZINC.

By H. PAWECK.

For the electrolytic estimation of zinc the author has adopted the following method:—

The cathode is formed of one or two discs of sheet copper, 6 cm. in diameter, suspended by a copper wire 10 cm. long and 1 m.m. diameter attached to the centre; when two discs are used they should be about 12 m.m. apart. The discs should be 0.5 m.m. in thickness. Before fixing the disc or discs to the wire they should be cleaned by rubbing them with wet chalk; they should then be washed with water and plunged for an instant in dilute sulphuric acid.

The cathode thus cleaned is amalgamated electrolytically once for all, by suspending it in a bath containing about 0.6 gm. of bichloride of mercury and 3 to 5 c.c. of concentrated nitric acid per 200 c.c. In one hour, with a current of 0.1 to 0.2 ampère, a sufficient deposit of mercury is obtained on the cathode. The electrode thus amalgamated is washed with dilute hydrochloric acid, then with water, alcohol, and ether, and finally dried and placed in an exsiccator.

The anode is formed of a perforated strip of platinum.

The electrolytic estimation can be made either in alkaline or acid solution. The author gives the results of a large number of analyses to show the value of the method. In these analyses the electrolyte, as a rule, has a volume of 200 c.c., and contains—

Alkaline Electrolyte.

0.16–0.51 gm. of Zn, as ZnSO_4 .
7–12 grms. of Seignette salt.
5–8 grms. of KOH or NaOH.

Acid Electrolyte.

0.23–0.31 gm. Zn, as ZnSO_4 .
14 grms. K_2SO_4 or Na_2SO_4 .
3–5 drops of concentrated H_2SO_4 .

The electromotive force employed is 3.6 volts. When the electrolysis is finished, the cathode is washed in distilled water, alcohol, and ether, dried at a low temperature, and weighed. The deposit of zinc can be easily redissolved in hydrochloric acid of medium strength.—*Zeit. f. Elektrochemie*, v., [18], 221.

ON BINOXIDE OF MOLYBDENUM.

By MARCEL GUICHARD.

It has been shown (*Comptes Rendus*, cxxv., pp. 25 and 105; *Bull. Soc. Chim.*, Series 3, xvii., p. 902), that when trioxide of molybdenum or molybdic anhydride is gradually reduced by means of hydrogen, no other oxide than the brown anhydrous binoxide is formed. Particularly it is noticed that, at no matter what temperature, reduction does not lead to the formation of definite oxides, such as Mo_5O_{12} , Mo_4O_5 , Mo_3O_8 , or $3\text{MoO}_2\cdot 2\text{MoO}_3$, $\text{MoO}_2\cdot\text{MoO}_3$, Mo_2MoO_2 . Several authors having described these compounds of the binoxide and the trioxide, that is to say, oxides intermediate between MoO_2 and MoO_3 , we have taken up the study of their preparation.

I. Action of Molybdic Anhydride on Molybdate of Ammonia.

When we heat a well-powdered mixture of 1 part of molybdate of ammonia and 2 parts of pure molybdic anhydride, for a few minutes before the blowpipe in a covered platinum crucible, until the mass is fused, we obtain a brownish-violet button with red, violet, and copper coloured iridescence; if the heating has not been too prolonged the surface of the button is covered with a grey metallic layer and flakes of sublimed molybdic anhydride; there is also a little sublimate on the cover of the crucible.

The experiment, repeated a large number of times, always leads to the same result.

Berlin (*Journ. f. Prakt. Chem.*, xlix., p. 444), thought that a molybdate of molybdic oxide was thus produced; to get rid of the excess of the molybdic oxide which enveloped it, he treated it with ammonia; he then obtained the compound Mo_3O_8 .

Uhrlaub (*Poggend. Ann.*, ci., p. 605), having shown that this oxide contains nitrogen, Muthmann (*Liebig's Ann.*, cxxxviii., p. 117), followed the treatment with ammonia, by a prolonged boiling with hydrochloric acid, to destroy the nitrated compound. He thus obtained an oxide with the composition Mo_5O_{12} , not attacked by alkaline solutions or dilute sulphuric and hydrochloric acids.

When we attempted, by this method, to dissolve the molybdic anhydride in ammonia we found that the operation was a very long one. In one experiment, the body resulting from the action of molybdic anhydride on molybdate of ammonia, washed several times with ammonia by decantation, and then dried at 110° , contained 72.59 per cent of the metal. After being treated for several days with ammonia, it contained 74.39 per cent of molybdenum, and was not then completely freed from free molybdic anhydride. It is thus very difficult to effect a complete purification by means of ammonia. This is caused by the fact, that though molybdic anhydride dissolves very rapidly in ammonia, when it has only been heated to a dull red heat, it takes a very long time to dissolve after it has been melted or sublimed. On the other hand, a solution of soda dissolves molybdic anhydride, after calcination, fusion, or sublimation, with very great rapidity.

We have therefore adopted the following treatment:—

The oxide to be purified is treated on the water-bath alternately with a solution of soda at 10 per cent; pure hydrochloric acid diluted with its own volume of water is then added until the hydrochloric acid is no longer coloured red, and the liquid, saturated with acetic acid, is no longer precipitated by acetate of lead.

The oxide thus obtained, dried at 110° , is of a brownish-violet colour and crystalline; the iridescence apparent before the purification has disappeared; it was due to a thin layer of melted molybdic anhydride enveloping each particle of oxide. Under the microscope it appears in the form of small crystals with numerous brilliant facets. It does not contain any nitrogen, and gives on analysis:—Molybdenum, 74.90 and 75.01 per cent; calculated for MoO_3 , 75 per cent. This oxide is therefore pure, crystallised binoxide of molybdenum.

The binoxide prepared by Bucholz's method, by heating the molybdate of ammonia alone, and then submitting it to the treatment as above described, has the same appearance, the same colour, and the same composition. On analysis it gave:—Molybdenum, 75.05 per cent.

II. Electrolysis of Melted Molybdic Anhydride.

Buff (*Liebig's Ann.*, cx., p. 275), in 1859, electrolysed melted molybdic anhydride in a U tube with platinum electrodes. The lower oxide produced, washed with ammonia, when analysed by Wöhler, had the composition Mo_3O_8 .

According to Muthmann, this body is not formed by the electrolysis of the pure oxide MoO_3 , and that obtained by Buff should contain nitrogen.

We have effected the electrolysis of molybdic anhydride in the following manner:—

The pure oxide, MoO_3 , is melted in a porcelain crucible covered with a lid of asbestos card; two electrodes of graphite, 8 m.m. in diameter, pass through this cover and conduct the current from five Bunsen cells through the melted mass. The electrolysis is continued for thirty minutes with a current of 10 ampères. The difference of potential between the electrodes is about 3 volts.

The crucible contains, after cooling, a brilliant grey-brown iridescent button, under a layer of sublimed oxide, MoO_3 . The electrodes do not show a trace of alteration. An experiment made with platinum electrodes gave the same result.

To prevent an abundant sublimation of molybdic anhydride, it is preferable to form the bath with molybdate of potassium, which gives the same results as molybdic anhydride alone.

The most convenient bath is obtained by the fusion of 15 grms. of the pure oxide, MoO_3 , with 20 grms. of carbonate of potassium; the molybdate formed corresponds as nearly as possible to the quintamolybdate, $5\text{MoO}_3\text{K}_2\text{O}$, and gives off but very little vapour of molybdic anhydride when melted at a red heat.

Under these conditions, we were able to prolong the electrolysis by an hour and a half, with a current of 3.5 ampères. The return is always small, for the reason that, as observed by Buff, the oxide formed being a good conductor of electricity, a moment arrives when the current passes without producing any sensible electrolysis; the disengagement of oxygen at the positive electrode then becomes almost nil.

The lower oxide formed, mixed with a large excess of MoO_3 , or melted molybdate of potassium, is treated with soda at 10 per cent until nothing more is dissolved; it is then treated with hydrochloric acid, water, and finally dried at 110° . There then remains a brilliant brownish-violet body, formed of an agglomeration of a large number of crystals. Analysis gives:—

	Electrolysis of molybdic anhydride	Electrolysis of molybdate of potassium.	Calculated for MoO_3 .
	Per cent.	Per cent.	Per cent.
Molybdenum..	74.95	74.83	75.00

This oxide is thus pure crystallised binoxide of molybdenum.*

The analysis of different samples of binoxide obtained by us, were made by two different methods:—

1. By oxidation of the oxide by means of dilute nitric acid, then desiccation and calcination below a dull red heat of the trioxide formed.

2. By the oxidation of the binoxide by means of dilute nitric acid and saturation of the molybdic acid formed by ammonia; the solution is then acidulated with acetic acid and precipitated with acetate of lead. The molybdate of lead dried, and moderately calcined, is weighed (Chatard's method).

These two methods are very exact. To sum up, the oxide produced by the calcination of a mixture of molybdate of ammonia and molybdic anhydride, is crystallised binoxide of molybdenum identical with that formed by the calcination of molybdate of ammonia alone.

On the other hand, the electrolysis of melted molybdic anhydride and molybdates of potassium also give the crystallised binoxide.

The result of this research shows that there is no other intermediate anhydrous molybdic oxide between the oxides MoO_2 and MoO_3 than the one produced by the dehydration of the blue hydrated oxide, if this dehydration can be effected without peroxidation.

We are about to examine this matter further.—*Bull. Soc. Chim.*, Series 3, xxi., No. 24.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 18th, 1899.

Professor THORPE, F.R.S., President, in the Chair.

MESSRS. E. W. Lewis, A. J. Shelton, S. Blofield, and J. N. Goldsmith were formally admitted Fellows of the Society

Certificates were read for the first time in favour of Messrs. Frederick Nolan Baker, 3rd Royal Inniskilling Fusiliers, Mullingar, Ireland; William Francis Cooper, Ashlyns Hall, Berkhamstead; Alexander Findlay, Emilienstrasse, 101, Leipzig, Germany; Julius Geldard, 120, Park View Terrace, Otley Road, Bradford; Adam Houston, Brisbane House, Bellahouston, Glasgow; Walter A. Riley, Brunswick Lodge, Newmarket Road, Norwich; Fred Pilkington Sargeant, Springfield Place, Leeds; Edward Shrapnell Smith, 35, Botanic Road, Wavertree Park, Liverpool, E.

Of the following papers, those marked * were read:—

*1. "Note on Nitrogen Halogen Compounds." By JULIUS STIEGLITZ and E. E. SLOSSON.

The authors point out that F. D. Chattaway and K. J. P. Orton, in their work on "A Series of Substituted Nitrogen Chlorides, &c." (*Trans.*, 1899, lxxv., 1046), have overlooked a series of papers emanating from the Kent Chemical Laboratory of the University of Chicago, in which, since 1893, results of work on the nitrogen halogen compounds in various directions have been given, and a definite line of work undertaken for further investigation. In one of these papers "Ueber die Einwirkung von unterbromiger Säure auf Saeureanilide" (*Ber.*, 1895, xxviii., 3265), the preparation and behaviour of acyl-phenyl nitrogen chlorides and bromides are discussed, and some of the compounds obtained by Chattaway and Orson described. In order to avoid future conflict, the line of work pursued by one of the authors and his students is fully outlined as centring in a study of the "Beckmann

* We shall, later on, give the results obtained by the electrolysis of other compounds of molybdenum.

rearrangement" of acyl-nitrogen halides and analogous bodies.

Further results are given concerning the behaviour of acyl-phenyl nitrogen halides, especially towards alkalis, potassium cyanide, and zinc ethide. All of these reagents reproduce acylanilides. The preparation of acyl-alkyl-nitrogen chlorides and representatives of the series are described: *ethyl benzoyl nitrogen chloride*, $C_2H_5NCl.COC_6H_5$, m.p. 53.5° , the corresponding methyl compound, is an oil. Alkalis, potassium cyanide, and zinc ethide regenerate the acyl-alkyl-amides.

Further representatives of the isomeric series, the chloro (or bromo) imido-acid esters, $RC(:NCl)OC_2H_5$, &c., are given; *chloroimidoethyl metanitrobenzoate*, $NO_2C_6H_4C(NCl)OC_2H_5$, m.p. 61° , the corresponding bromide melts at 71° ; the analogous *chloroimide of β -naphthoic ethyl ether* melts at 68° , the bromide at 77° . These ethers are remarkably stable nitrogen halides, perhaps the most stable known. Some have been distilled without decomposition in a vacuum above 100° ; boiling alcoholic ammonia does not decompose chloroimidoethyl-metanitrobenzoate. Although a number have been obtained in solid form, no stereoisomeric compounds, $RC(NCl)OR$ have as yet been observed, such as exist in the case of the analogous benzhydroxamic ethers, $C_6H_5C(:NOH)OC_2H_5$. On treatment with zinc ethide, ethylamine derivatives are obtained.

DISCUSSION.

Dr. CHATTAWAY said he regretted that the papers mentioned had been at first overlooked. Dr. Orton and he had approached the subject from an entirely different point of view, and he did not think that their future work was likely to overlap. Professor Stieglitz and his students were working on the Beckmann change, while they were chiefly studying substitution, and endeavouring to show that the chlorination and bromination of anilines and anilides are not direct processes, but that nitrogen chlorides and bromides are always first formed, and under favourable circumstances subsequently undergo isomeric change.

*2. "On the Electrolysis of the Nitrogen Hydrides and of Hydroxylamine." By E. C. SZARVASY, Ph.D.

A short account was given of the experiments of the author on the electrolysis of solutions of ammonia, hydrazine, azoimide, hydroxylamine, and of their salts.

The experiments were carried out at different temperatures, and with varying current densities and concentrations. The conditions were determined under which ammonia, hydrazine, and azoimide, on electrolysis, yield their two components in the proportions contained in their molecules respectively, and without the formation of any secondary products.

In the case of hydroxylamine and its salts, both oxidation and reduction products were formed, no matter how the experimental conditions were varied.

Many attempts were made to prepare polymeric nitrogen by electrolysing solutions of azoimide and its salts at very high current densities; this part of the work is still in hand.

*3. "On the Relationship between the Constitution of some Substances and the Fluorescence which they exhibit." By J. T. HEWITT, M.A., D.Sc.

Since fluorescence is the absorption of radiant energy of definite wave-length or wave-lengths, and emission of the same energy after it has been reduced in vibration-frequency, one would expect to find fluorescence usually a

property of substances capable of existing in tautomeric forms. As a matter of fact, the colouring-matters which do exhibit fluorescence are almost without exception tautomeric, the exceptions which are known being usually substances for which no very great degree of purity can be guaranteed.

But many substances which behave tautomerically do not exhibit well-marked fluorescence; this might well be due to the fact that in a solution in which the two tautomeric forms are in equilibrium the reaction velocities from one form to the other are so small that a very few of the molecules have the opportunity of absorbing energy when they correspond to one and emitting it in the other configuration.

The case is, however, very different when the molecule in one of its configurations is symmetrical; to pass from this to the other configuration, either of two displacements is necessary, equal in magnitude, but opposite in direction. Just as a pendulum (neglecting the friction due to its support and the medium in which it vibrates) swings regularly between two extreme positions, passing at regular intervals through its lowest point, so a molecule of a substance which exhibits the kind of tautomerism characteristic of fluorescein might undergo continual and frequent change. Fluorescein itself yields derivatives, not only of a phenolic lactone, but also of a quinone-carboxylic acid. The transition from the lactone to the quinone-carboxylic form may be effected by displacement of either of its phenolic hydrogen atoms, the symmetry of the molecule conditioning the equality of energy necessary for displacement of either atom. Hence all the molecules will be undergoing tautomeric change continuously and frequently, and energy absorbed when the molecules have one configuration will be, to an appreciable extent, emitted when they correspond to the other configuration. It is practically certain that the vibration frequency of fluorescein is different in the two states (the diethyl ethers corresponding to the two forms are quite different in the character of their absorption), and hence every opportunity is offered for energy of a rapid vibration frequency to be largely transformed into energy of greater wave-length.

In the case of fluorescein, the condition of a molecule may be symbolised in the manner shown below.

The greater number of fluorescent dye-stuffs conform to the theory shortly stated above; exceptions may, however, be classed under two heads:—

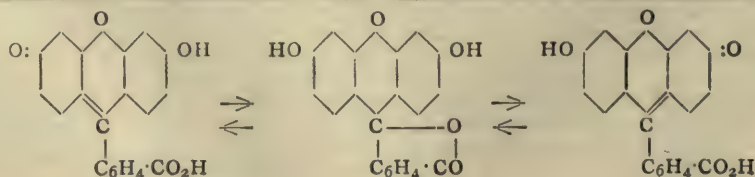
(i.) Substances having the requisite structure, but not exhibiting fluorescence.

(ii.) Substances exhibiting fluorescence, but not possessing the doubly symmetrical tautomeric structure considered in the case of fluorescein.

It is, however, probable, that many of the exceptions are only apparent, the fluorescent spectrum not having been sufficiently examined.

4. "Action of Fuming Nitric Acid on α -Dibromocamphor." By ARTHUR LAPWORTH and EDGAR M. CHAPMAN.

The authors have repeated the work of Kachler and Spitzer on the oxidation of α -dibromocamphor (*Monatsh.*, 1883, iv., 554), and agree with them that camphoronic acid is produced, but the quantity of this substance is small, and it is difficult to separate it from homocamphoronic acid, which is present in much larger amount; on the other hand, they have not been able to detect any isocamphoronic acid, and conclude that Kachler and



Spitzer were merely dealing with impure homocamphoronic acid.

The product, to which Kachler and Spitzer gave the provisional formula $C_{24}H_{33}BrN_4O_{12}$, appears to have been a mixture of the substance $C_{10}H_{16}N_2O_6$, already described by the authors (*Trans.*, 1899, lxxv., 986), with ordinary nitrobromocamphor, $C_{10}H_{14}OBrNO_2$, produced by the nitration of monobromocamphor formed in the initial stage of the reaction.

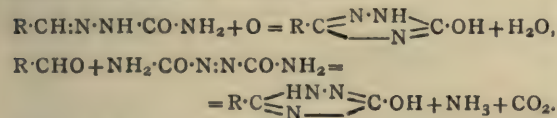
Besides the above-mentioned products and dibromocampholide, a number of other substances seem to be formed. One of these remains dissolved in the water with which the mixture is diluted, and cannot be isolated by dilution. It is obtained by extracting the liquid containing the homocamphoronic acid with chloroform, and forms a neutral oil which is not readily soluble in pure water; it is probably a lactone. When this substance is allowed to remain with aqueous potash, it produces an acid having the formula $C_{10}H_{16}O_4$, which forms magnificent transparent crystals, is sparingly soluble in water, and melts at 177° . When distilled, or warmed with strong acids, it undergoes a curious molecular change, yielding an acid, $C_{10}H_{12}O_4$, melting at $167-168^\circ$, which has been identified as trimethylbenzoic acid, $(CO_2H : Me : Me :: 1 : 2 : 3 : 4)$.

5. "Note on Volhard's Method for the Assay of Silver Bullion." By T. K. ROSE, D.Sc.

The precautions to be observed in using the method are described, and the limit of accuracy put at 0.1 per 1000, instead of 0.25 per 1000, as stated by Van Riemsdyk.

6. "c-Substituted Hydroxytriazoles." By GEORGE YOUNG, Ph.D., and ERNEST WITHAM, B.A. B.Sc.

The authors have prepared hydroxytriazoles by two actions represented by the equations—



Where R is the same group, the products of the two actions are apparently identical.

c-Phenylhydroxytriazole, $C_6H_5 \cdot C_2N_3H_2O$, m. p. $321-322^\circ$. Forms two silver salts, $C_6H_5 \cdot C_2N_3HO \cdot Ag$ and $C_6H_5 \cdot C_2N_3O \cdot Ag_2$. Acetyl derivative,—

$C_6H_5 \cdot C_2N_3HO \cdot C_2H_3O$,
m. p. 248° . c-Metanitrophenylhydroxytriazole,—
 $NO_2 \cdot C_6H_4 \cdot C_2N_3H_2O$,

m. p. 304° . Forms two silver salts, $C_8H_5N_4O_3Ag$ and $C_8H_4N_4O_3Ag_2$. Acetyl derivative, $C_8H_5N_4O_3 \cdot C_2H_3O$, m. p. $261-262^\circ$. Cinnamalsemicarbazone,—

$C_6H_5 \cdot CH : CH \cdot CH : N \cdot NH \cdot CO \cdot NH_2$,
m. p. $215-216^\circ$. c-Styrenylhydroxytriazole,—
 $C_6H_5 \cdot CH : CH \cdot C_2N_3H_2O$,

m. p. 311° . Forms two silver salts, $C_{10}H_8N_3OAg$ and $C_{10}H_7N_3OAg_2$. Monoacetyl derivative, $C_{10}H_8N_3O \cdot C_2H_3O$, m. p. $241-242^\circ$. Diacetyl derivative, $C_{10}H_7N_3O \cdot (C_2H_3O)_2$, m. p. $137-138^\circ$.

7. "Note on the Use of a Mixture of Dry Silver Oxide and Alkyl Halides as an Alkylating Agent." By G. DRUCE LANDER.

Dry silver oxide and alkyl iodides have been employed in the preparation of the ethereal salts of alkyloxy-acids (*Trans.*, 1899, lxxv., 157, 485, 754). The use of the method in the preparation of alkyl derivatives of compounds of other classes has been studied. Optically active ethyl menthyl ether has been prepared by the action of dry silver oxide and ethyl iodide on l-menthol. The optically active ether is an oil boiling at $207.5-209.5^\circ$ (uncorrected); $d_{20}^{20}/4^\circ = 0.8537$; $[\alpha]_D^{20} = -98.32^\circ$.

The ethyl and isopropyl ethers of benzoin are obtained

by the action of silver oxide and ethyl and isopropyl iodides respectively on benzoin. The ethyl ether crystallises from light petroleum in needles melting at $58-58.5^\circ$; compare Limpricht and Jena (*Annalen*, 1870, clv., 96), and Fischer (*Ber.*, 1893, xxvi., 2415). The isopropyl ether, of similar crystalline form, melts at $72-75^\circ$.

The action of silver oxide and ethyl iodide on benzamide leads to the formation of ethyl benzimido ether. The hydrochloride melts at $119-120^\circ$ with evolution of gas; compare Pinner (*Ber.*, 1883, xvi., 1654), and Tafel and Enoch (*Ber.*, 1890, xxviii., 103).

The introduction of one ethyl group in place of hydrogen in ethyl acetoacetate can be readily effected by the aid of silver oxide and ethyl iodide. The product consists of ethyl ethylacetoacetate containing, however, approximately 2 per cent of ethyl β -ethoxycrotonate, melting at 30° , and yielding on hydrolysis ethoxycrotonic acid which melts at 137.5° , with evolution of gas. The introduction of an ethyl group into ethyl ethylacetoacetate, and ethyl malonate by the same method, is also possible, but the proportion of the ethyl homologue obtained is small. No indication could be obtained of the production of the ethyl homologue of ethoxycrotonic acid by the action of silver oxide and ethyl iodide.

Ethyl acetosuccinate may be prepared by the action of silver oxide and ethyl iodoacetate upon ethyl acetoacetate.

Further results and details will be given in a subsequent communication.

Victor Meyer Memorial Lecture.

The Victor Meyer Memorial Lecture will be delivered by Professor T. E. Thorpe, F.R.S., President of the Society, on the evening of Thursday, February 8th, 1900, at 8.30.

PHYSICAL SOCIETY.

Ordinary Meeting, January 26th, 1900.

Prof. LODGE, F.R.S., President, in the Chair.

A PAPER by Prof. AYRTON and Mr. MATHER on "Some Developments in the use of Price's Guard Wire in Insulation Tests," was read by Prof. Ayrton.

For insulation tests made by the direct deflection method the guard-wire properly applied affords complete protection against surface leakage when the ends of the cable tested are near the galvanometer, so that it is possible to have the wire connecting the conductor of the cable with the galvanometer terminal "air insulated." A difficulty, however, arises when the ends of the cable are at a considerable distance from the testing instrument; this may render air insulation impossible. The authors have overcome this difficulty by applying a guard-wire along the entire length of the lead. This is done by using a concentric wire to connect the cable and galvanometer, the inner of the concentric being used as the lead, and the outer as the guard-wire. The principle can also be applied to determine whether a defective piece of cable is bad throughout, or bad owing to one or more isolated faults. In this case the cable is placed in two water-tanks, one of which is earthed, and the other fairly well insulated. By a suitable arrangement of the guard-wire it is then easy to determine the resistance of the wire in the earthed tank, so that by altering the length of this wire the character of the insulation can be determined throughout the whole length of the cable. In referring to some of the earliest experiments with the guard-wire made by Mr. Appleyard in 1895, Prof. Ayrton pointed out that the principle had not been applied completely, and that at one point there was a chance of leakage.

Mr. CAMPBELL said that the necessity of having a concentric could be obviated by simply hanging the lead from the guard-wire by short lengths of material of fair insulation.

Mr. APPELYARD said that he quite agreed with Prof. Ayrtton that the guard-wire ought in general to be applied at both ends of all leads, provided that both ends could be got at. The reason it was used at one end only in the experiments on dielectrics, made in 1895, was that the far end of the lead was carried into the condenser box, which was submerged in water in the temperature tank. Special precautions were taken to ensure good insulation of the submerged end of the lead, and tests showed that the leakage there was nil. As the end of the wire could not be got at, no guard-wire could be applied. Mr. Appleyard congratulated the authors upon the use of a concentric cable for a lead, and pointed out that such a lead was sufficient for all the routine tests on core; the inner and outer conductors could be used for the purpose of taking the "copper" resistance.

Mr. PRICE expressed his interest in the developments of his principle which had been made by the authors.

Mr. APPELYARD then read a paper on "*A Fault-test for Braided and other Cable-core.*"

This method enables the fault to be found without the removal of braiding or tape. The core is wound on two insulated drums or tanks, the intermediate piece of cable being about ten feet long. One end of the core is left free, the other is connected to earth through a galvanometer and a battery. A guard-wire is connected from some point between the galvanometer and the battery to some point of the braiding on the wire between the drums. A wet cloth, connected to an earth wire, is laid on one or other of the drums, over the braiding. The galvanometer deflection is noted. The earth-wire is then changed over to the second drum, and the corresponding deflection is observed. A comparison of these deflections at once indicates upon which drum the fault lies. With the galvanometer still deflected the core may be run through a suitable contact brush or sponge attached to the guard-wire. The instant the fault passes under the guard-wire contact, the deflection falls and the fault is located. The paper gives the theory of the method, and indicates how to apply it (1) to localising "distributed" faults; (2) to several faults in a single cable; and (3) to the case of a single fault. One advantage of the method is that at the critical moment when the fault passes under the guard-wire the galvanometer is short-circuited through the fault and thus completely protected.

A paper on "*Reflection and Transmission of Electric Waves along Wires,*" by Dr. E. BARTON and Mr. L. LOWNDS, was read by Dr. Barton.

The waves used were produced by means of an induction coil and an oscillator, and travelled along wires 0.15 c.m. diameter, 8 c.m. apart, and 166 metres long. The ends of the wires were connected by graphite markings on ground glass, so that any wave trains which reached the ends were at once absorbed. Three circular parallel-plate condensers were used of 15, 9, and 5 c.m. radius respectively. The plates were, in all cases, separated by air, and were placed 1 c.m. apart. The needle of the electrometer connecting the wires was uncharged, so that it was always attracted by the charged plates. The positions of the condenser and electrometer could be varied so as to study either the reflected or the transmitted waves. The electrometer produced a negligible disturbance, as it reflected only 0.04 per cent of the energy incident upon it. The authors have attacked the problem mathematically, using the relations of Heaviside, and have obtained expressions for the reflected and transmitted systems. These expressions consist of two terms, one of which is comparatively unimportant. From the other term certain values have been calculated. A superior limit has then been given to the other term, and the values already obtained have been subjected to a correction on this account. By a suitable arrangement of the condenser and electrometer these calculated values have been experimentally determined, and are in close agreement with the theoretical numbers, falling in many cases between

the results derived from the approximate and the corrected theories. The authors have also investigated the stationary wave system produced by interference when the electrometer is placed close to the condenser, and between the condenser and the oscillator.

The CHAIRMAN said that the experiments afforded a satisfactory verification of Heaviside's theory.

A paper on "*The Frequency of Transverse Vibrations of a Stretched Indiarubber Cord,*" by Mr. T. J. BAKER, was taken as read.

In this paper Mr. Baker has investigated the frequency of the note given out by an indiarubber cord of square section when subjected to different tensions. The relation between length and tension is linear over a considerable range. The curve connecting length with frequency shows that while the cord was doubling its length the pitch was rising rapidly, but that further extension was practically without effect. Since the relation between length and tension is linear, while the sectional area is decreasing, it follows that the value of Young's modulus must be changing. The author has shown that the value of Young's modulus is proportional to the square of the stretched length of the cord. Using this fact the frequency of the note given out by a stretched indiarubber cord is shown to be proportional to a quantity which varies very slightly with increase in length of the cord, and hence the variation of elasticity is given as the cause of the constancy of the note.

Mr. APPELYARD exhibited some Mirrors produced inside incandescent electric lamps by the application of voltages much above those for which the lamps were designed, and the consequent deflagration of the filaments.

The meeting then adjourned until February 9th.

NOTICES OF BOOKS.

The Analysis of Food and Drugs. Part II. The Chemical and Biological Analysis of Water. By T. H. PEARMAIN and C. G. MOOR, M.A. London: Baillière, Tindall, and Cox. 1899. Pp. 172.

NATURAL waters, generally speaking, may be arranged in the following order with regard to purity:—(1) Rain-water collected under proper conditions; (2) Deep spring and artesian-well water; (3) upland surface waters; (4) subsoil water; (5) rivers water; (6) land springs; and (7) surface water from cultivated lands. The impurities found in water which affect its potability are mainly the products of decomposition of animal and vegetable matter, and also suspended matter, either living or dead, in the form of algæ, moulds, bacteria, insects, &c. Of late years less importance has been given to merely chemical results in the examination of water, while the value and importance of biological and bacterial examination cannot be over estimated. A water must not be condemned simply because it contains a high proportion of organic matter, if the bacteriological results show that only a small number of harmless microbes are present; and it must be further remembered that there may be distinct danger in carrying the bacterial purification of water too far; certain microbes act as policemen, so to speak, and are able to destroy pathogenic microbes introduced in small numbers. If, however, the police microbes become too few in number, the injurious ones increase at an enormous rate, and danger of an epidemic of disease is the immediate result.

The authors devote a considerable portion of their book to the chemical analysis of water, many of the various methods in vogue being well and clearly described, though we are sorry to see that very little space is devoted to Frankland's combustion process, which is unrivalled for the estimation of the organic carbon and nitrogen in water.

The bacteriological examination of waters is also soundly dealt with, the authors being known as authorities on this subject.

Altogether this book, dealing as it does with both the chemical and bacteriological branches of the subject, combines in one volume an amount of information that cannot fail to be of much service to those interested in the subject.

The Production of Tin. By HENRY LOUIS, M.A., A.R.S.M., &c., Professor of Mining, Dutham College of Science. London: *The Mining Journal*. Pp. 39.

THE articles forming this volume were originally written for *The Mining Journal*, but are now presented in book form. They give a history of the production of tin from early times up to the present day.

Tin is by far the rarest of the common metals, and is produced in much smaller quantities than any of the others; it is but sparsely distributed throughout the world, and is only found in paying quantities in a few localities, such as Cornwall, Saxony, Spain, Bolivia, the Malay Peninsula, and Australia. It may be noted that tin is the only common metal besides iron, the only true ore of which is the oxide; it is, therefore, easily treated for producing the metal. Tin is reduced either in the blast-furnace or in the reverberatory furnace; the former is, however, probably responsible for 60,000 out of the world's approximate total of 80,000 tons. The relative importance in production of the different tin bearing districts is shown by the following figures:—

Straits Settlements	60.6 per cent
Netherlands, East Indies	19.0 "
Australasia	7.9 "
Cornwall	6.1 "
Bolivia	6.0 "
Other minor producers	0.4 "

100.0

It is to be hoped that before long a payable method of recovering tin from scraps and cuttings of tin-plate will be discovered. Such a process would materially help to diminish the price of the metal. There is also room for improvement in the methods in use for producing tin, in fact it is shown that there has been less progress in the metallurgy of tin than in that of any other metal; the best hopes for the future must, therefore, lie in the successful application of modern science to all branches of the industry, from mining to refining.

CORRESPONDENCE

PHYSICAL EQUILIBRIUM OF MOLECULAR SYSTEMS.

To the Editor of the Chemical News.

SIR,—In my letter to last week's *CHEMICAL NEWS* I suggested an explanation of the "Double Centre of Stability" of Si_2Cl_6 . My friend Mr. T. Beacall, however, has called my attention to the fact that if there was present an impurity in the Si_2Cl_6 , it may happen that this impurity would react with the Si_2Cl_6 between the limits 350–800°, and thus cause its dissociation, much in the same way that H_2O dissociates NH_4Cl vapour. Above 800° C. this impurity might itself be decomposed by the heat, and would thus cease to decompose the Si_2Cl_6 . This would explain the stability of the Si_2Cl_6 above 800°.

It would therefore be advisable to repeat the experiments with absolutely pure Si_2Cl_6 , and see whether an analogous phenomenon occurs with the pure product.—I am, &c.,

GEOFFREY MARTIN.

13, Hampton Road, Bristol.
January 22nd, 1900.

RELATIONS BETWEEN THE ATOMIC WEIGHTS AND PHYSICAL PROPERTIES OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—In the *CHEMICAL NEWS* (lxxx., p. 282) there appears a note from Mr. Thomas Bayley, pointing out that the product of melting point (absolute) $\times$ coefficient of expansion for 1° C. is a constant for a number of elements.

In a paper I read before the Physical Society in June, 1895 (*CHEM. NEWS*, lxxi., p. 303), I brought forward the same relation, limiting the constancy of the product to elements in the same periodic group: about the same time Pictet proposed a similar relation, but introduced into the equation the cube root of the atomic volume, and applied the relation generally to all the elements.

I published a second paper in the *CHEMICAL NEWS* (lxxvi., p. 81), wherein I attempted to collate and criticise work that had been done by myself and other workers on this and some other allied relations.—I am, &c.,

NOEL DEERR.

26, South Parade, Chelsea, S.W.,
January 23rd, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 2, January 8, 1900.

Application of the Law of Phases to Alloys and Rocks.—H. Le Chatelier.—By applying Gibbs's law of phases to a mixture of solid bodies taken at ordinary temperatures, and obtained by a succession of reversible transformations, such as solidification by freezing or crystallisation from solution, the author arrives at the following conclusion:—The stable state of a solid mixture (melted salts, metallic alloys, rocks, &c.), corresponds to a monovariant system—that is to say, that the number of phases should be equal to the number of independent constituents which enter into its composition.

Rhodicyanides.—E. Leidié.—The author attempted to reproduce cyanide of rhodium and potassium, first by the dry method and then by the wet method, in order to verify Marius's work. He found that the double cyanide crystallises in monoclinic prisms, slightly tinted yellow. These are anhydrous and extremely soluble in water. The nitrogen was estimated by an elementary analysis, the potassium by transformation into the chloride (calcination with NH_4Cl in a current of hydrogen), and the rhodium by electrolysis (after decomposition of the salt with H_2SO_4). This analysis leads to the numbers Rh : Cy6 : K3, possibly $\text{Rh}_2\text{Cy}_{12}\text{K}_6$. This latter formula has been proved by other considerations.

New Micro-chemical Reactions of Copper.—M. Pozzi-Escot.—By using crystallised cupric iodide the author obtained ammoniacal compounds which are very characteristic. First, the iodide, $\text{CuI}_{2.4}\text{NH}_3 \cdot \text{H}_2\text{O}$, which appears under the microscope in the form of little blue tetrahedra, and which salt was obtained by treating a cuprous ammoniacal solution with ammonium or sodium iodide. Secondly, a dissociable compound, of which the exact composition has not been obtained, but which appears to have the formula $\text{CuI}_{4.4}\text{NH}_3$, which can be prepared by adding the cupric solution to a quantity of ammonia, sufficient to bring the temperature up to the point of dissolving the copper hydrate (at about 40°); iodide of sodium or ammonium is then added. Under these conditions the liquor immediately becomes yellowish green and deposits rhombohedral tables of a very dark brownish black.

Action of the Magnetic Field on Becquerel Rays. Rays Deviated and Rays Undeviated.—P. Curie.—The author shows that the rays of radium are composed of two well defined groups, those which are deviated by a magnetic field and those which are not. The non-deviable rays appear to be quite analogous to the rays of polonium.

Penetration of Becquerel Rays Non-deviable by the Magnetic Field.—M^{me}. Sklodowska Curie.—The non-deviable rays are much less penetrating than the deviable rays. A more complete study of the penetration of the two kinds of rays across various substances show that their nature is entirely different, and confirms the results obtained by the examination of the effect of the magnetic field.

MISCELLANEOUS

The Huddersfield Town Council at their meeting voted Mr. Edward A. Harman, M.Inst.C.E., the Gas Engineer, an increase of salary of £100 per annum from January 1st this year, with an additional £100 increase on January 1st, 1901.

Estimation of the Available Molybdenum in Molybdenite.—H. Bornträger.—One grm. of the mineral is digested for two hours with 25 c.c. of concentrated nitric acid in an Erlenmeyer flask. The molybdic acid formed is re-dissolved in ammonia, the solution is filtered, and the residue again treated with nitric acid and ammonia. The filtrates are added together, acidulated with nitric acid, and evaporated to dryness. The dry residue is digested with alcohol at 50 per cent, which dissolves the nitrate of ammonia, and leaves the molybdic acid intact. The latter is collected on a tared filter, and weighed. It may also be dissolved in normal ammonia and estimated by titration.—*Zeit. Anal. Chem.*, xxxvii., p. 438.

Estimation of Sulphur in the presence of Iron (Pyrites).—O. N. Heidenreich.—To prevent the carrying down of ferric sulphate by sulphate of barium precipitated in a solution rich in iron, the author proposes to first reduce the iron by means of metallic zinc before proceeding with the precipitation of the sulphuric acid. The ferrous sulphate thus formed is not carried down. The sample of pyrites to be examined is attacked in the ordinary manner with aqua regia, and the solution obtained is diluted to about 250 c.c., and a certain quantity of zinc added. After complete decolouration the solution is rapidly filtered and made up to 600 c.c.; it is then heated to boiling and precipitated with a boiling solution of chloride of barium.—*Zeitschr. Anorg. Chem.*, 1899, xx., p. 233.

Estimation of Zinc and Manganese in the State of Sulphides.—E. Murmann.—The estimation of zinc and manganese by precipitation as sulphides and calcination of the precipitates in a current of hydrogen gives good results, but requires very careful manipulation on account of the difficulty experienced in obtaining a clear filtrate, and also on account of the long time necessary for washing. If the precipitation is carried out in the presence of bichloride of mercury, the finely divided sulphide of zinc or manganese is carried down with the sulphide of mercury, and deposited very rapidly. The filtration and washing are also very rapid; if the precipitate is not very abundant the pores of the filter may be first filled up with a little sulphide of mercury. On calcining the sulphide of mercury is completely volatilised, and the residue consists of perfectly pure sulphide of zinc or manganese.—*Monatsh. für Chem.*, xix., [7], 404.

Patera's Method for the Estimation of Uranium.—H. Bornträger.—Patera's method for the estimation of uranium in its ores is as follows:—The mineral is dissolved in nitric acid, the solution is diluted, saturated with carbonate of soda, heated to boiling, and filtered.

The uranium is precipitated in the clear liquid by means of caustic soda; the precipitate of uranate of soda is collected and weighed as such. According to the author, this method, although sufficiently exact in the case of pure minerals, gives results which are much too high, in the case of samples rich in silica, as the precipitate will then contain a considerable proportion of silicic acid. The precipitate must in such a case be treated with hydrochloric acid, evaporated to dryness, taken up with dilute hydrochloric acid, filtered, and the uranium in the clear liquid reprecipitated by means of caustic soda or ammonia.—*Zeit. Anal. Chem.*, xxxvii., p. 436.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.**—Society of Arts, 8. (Cantor Lectures). "The Nature and Yield of Metalliferous Deposits," by Bennett H. Brough.
— Society of Chemical Industry, 8. "On Recent Objections urged against the Adoption of the Metric System," by Dr. W. S. Squire, F.I.C., F.C.S. "Oil of Carthamus Tinctorius (Safflower Oil)," by H. R. Le Sueur.
— Royal Institution, 5. General Monthly Meeting.
- TUESDAY, 6th.**—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
- WEDNESDAY, 7th.**—Society of Arts, 8. "Housing of the Poor," by Edmund Wilson.
— Society of Public Analysts, 8. "Note on the Separation of Oleic Acid from other Fatty Acids," by J. Lewkowitsch, Ph.D., F.I.C. "Analysis of a Sample of 'Treacle' and of a Sample of so-called 'Golden Syrup,'" by C. G. Matthews, F.I.C., and A. Hyde Parker. "The Determination of Carbon and Sulphur in Steel," by Bertram Blount, F.I.C. "Note on Sour Milk," by H. Droop Richmond, F.I.C., and J. B. P. Harrison. "Butters from various Countries Compared," by C. Estcourt, F.I.C.
- THURSDAY, 8th.**—Royal Institution, 3. "Modern Astronomy," by Prof. H. H. Turner, M.A., F.R.S.
— Society of Arts, 4.30. "New Projects of Railway Communication with India," by James Mackenzie Maclean, M.P. (This meeting will be held at the Imperial Institute).
— Chemical, 8.30. Victor Meyer Memorial Lecture, by Prof. T. E. Thorpe, F.R.S., President.
- FRIDAY, 9th.**—Royal Institution, 9. "Symbiosis and Symbiotic Fermentation," by Prof. J. Reynolds Green, S.C.D., F.R.S.
— Physical, 5. (Annual General Meeting). Address by the President, Prof. O. J. Lodge, D.Sc., F.R.S.
- SATURDAY, 10th.**—Royal Institution, 3. "The Idea of Tragedy in Ancient and in Modern Drama," by W. L. Courtney, M.A., LL.D.

THE DAVY FARADAY RESEARCH LABORATORY OF THE ROYAL INSTITUTION.

Directors:
The Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S.
Professor DEWAR, M.A., LL.D., F.R.S.
Superintendent of the Laboratory:
Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

The Laboratory is open free of charge to Workers of either sex, and any nationality, prosecuting individual investigations; and the extensive collection of Physico-Chemical Apparatus presented by the Founder is available for their use, together with such materials, chemicals, electricity, &c., as the Directors may authorise.

Assistants and a trained mechanician are attached to the Laboratory to aid Workers in the prosecution of their researches.

All persons desiring to be admitted as Workers must send evidence of scientific training, qualification, and previous experience in original research, along with a statement of the nature of the investigation they propose to undertake.

MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

LENT TERM.—Monday, January 8, to Saturday, Apr. 7.

EASTER TERM.—Monday, April 30, to Saturday, July 28.

Forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

THE CHEMICAL NEWS.

Vol. LXXXI., No. 2098.

ON THE BEHAVIOUR OF THE BECQUEREL AND RÖNTGEN RAYS IN A MAGNETIC FIELD.*

By the Hon. R. J. STRUTT, B.A., Scholar of Trinity College, Cambridge.

In the current number of *Wiedeman's Annalen* an experiment is described by Giesel showing that the Becquerel rays are deflected in a magnetic field. This result is of great interest, on account of the light which it throws on the nature of the rays. Up to the present, the evidence has tended to show that the Becquerel rays were of the same nature as the Röntgen rays, both being capable of penetrating thin metal sheets, of affecting a photographic plate, and of producing ionisation in the surrounding air. Neither could be refracted or reflected, and, so far as as yet appeared, neither could be polarised.

These facts seemed to form a fairly strong body of evidence that the two kinds of radiation were essentially similar. But the announcement of the magnetic deflection of the Becquerel rays seems to throw doubt on this conclusion. The Röntgen rays, so far as is known, are quite unaffected by magnetic force. Under these circumstances it seemed worth while to make a new attempt to discover such an effect on the Röntgen rays. This attempt I have carried out. It will be best to say at once that the result is negative.

A focus tube was employed as the source of radiation. It was placed at a distance of about 35 c.m. from a powerful electro-magnet, and in such a position that the cathode rays in the tube were parallel to the magnetic force due to the magnet. The line joining the oblique anti-cathode to the centre of the magnetic field lay in the plane of the anti-cathode.

A short distance in front of the magnet a wire was placed at right angles to the direction of the rays, and in the plane of the anti-cathode. It was thus at an angle of about 50° to the magnetic force—the same angle as that between the axis of the cathode stream and the anti-cathode. This wire was used to cast a shadow on a photographic plate placed at a distance of 65 c.m. on the other side of the magnet.

An exposure was first made with the magnetic force in one direction. The exposure was then stopped, the field reversed, and another exposure given, of course without shifting the plate. If then the rays had been appreciably deflected, the photograph should have shown two shadows, either overlapping or altogether separated.

The rays casting the shadow were those emitted at a grazing angle from the anti-cathode. The reason for using these very oblique rays was that, owing to the foreshortening of the anticathode, the source was virtually narrower than it would have been had rays been used which left the anti-cathode at a greater angle. Thus sharper shadows were obtained, and a smaller magnetic deflection could have been detected.

The tube was arranged with its cathode stream parallel to the magnetic field, so as to avoid any shifting of the source of radiation when the magnet was reversed, owing to an effect of the magnet on the original cathode beam. Such a shifting would have given rise to a spurious effect. The only objection to this was that the shadow-casting wire had to be obliquely placed so as to be in the plane of the anti-cathode. Thus some sensitiveness was lost.

I shall now give an estimate of the smallest deflection which could have been detected. The rays traversed a distance of 65 c.m. after leaving the magnetic field.

It was estimated that a lateral displacement of the shadow of the wire by 0.02 c.m. could have been detected. But the wire was inclined 50° to the resultant magnetic force. Thus the smallest lateral displacement that could with certainty be detected was—

$$\frac{0.02}{\sin 50} \text{ c.m.}$$

The smallest angular deflection of the rays which could be detected would be, in circular measure,—

$$\frac{0.02}{65 \sin 50} = 0.000405.$$

The length through which the rays were exposed to the magnetic force was 8 c.m. If in this distance they were bent through the above angle, the radius of curvature would be—

$$r = \frac{8}{0.000405} \text{ c.m.} = 19,800 \text{ c.m.}$$

The strength of the magnetic field was determined in the usual manner, by observing the throw of a galvanometer when a small coil of known dimensions connected up with it was suddenly withdrawn from the region between the pole pieces. To reduce the results to absolute measure, the throw due to reversal of an earth-inductor in the same circuit was observed.

In this way the strength of the field was found to be

$$3270 \text{ C.G.S.}$$

It is convenient to exhibit the result by giving the maximum field which the experiments indicate as unable to produce a curvature of radius 1 c.m.

Since a field of 3270 does not produce a curvature of radius less than 19,800 c.m., we see that the field required to produce a curvature of radius 1 c.m. cannot be less than

$$6.5 \times 10^7.$$

Owing to the fact that the magnetic field was reversed instead of being merely shut off, the experiment is really of double the sensitiveness indicated above. But, in order to be well on the safe side, it has been thought best to leave this out of account.

For the sake of comparison I have attempted a rough estimate of the amount of the magnetic deflection of the Becquerel rays. The method employed was as shown in Fig. 1.

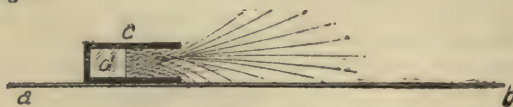


FIG. 1.

A photographic plate, shown in section at *ab*, was laid on the top of the square pole-pieces of a magnet, the magnetic force being perpendicular to the plane of the diagram. The plate was covered with thin aluminium foil; *c* is a metal capsule filled with the substance *d*, which emitted the rays.*

When no magnetic force was acting, the rays were emitted from the capsule as indicated in Fig. 1, some of some of them striking obliquely on the plate. On development after one hour's exposure, a shadow was obtained beginning at the edge of the capsule *c*, and extending a short distance. The effect gradually tailed off, and at a few c.m. distance away from *c* it was inappreciable. When the magnetic force was in such a direction as to bend the rays down into the plate (Fig. 2), the shadow extended further. When, on the other hand, the magnet

* The substance employed was a preparation from uranium residues, supplied by de Haen, Hamburg.

was reversed so as to bend the rays away from the plate (Fig. 3), the shadow obtained on development was much



FIG. 2.

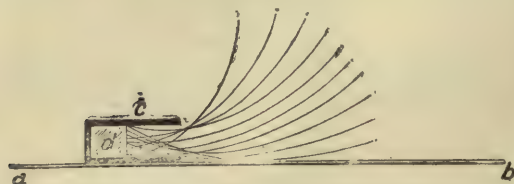


FIG. 3.

shorter, the time of exposure being, of course, in each case the same.

The numerical estimate of the curvature of the rays was obtained from an experiment of the latter kind.



FIG. 4.

Let us suppose that ec (Fig. 4) represents in section the front surface of the radiating substance, cf the surface of the photographic plate.

Let f be the place furthest from c at which the darkening on the photographic plate was perceptible. Now the rays which reach furthest are those which proceed from e , the highest point of the radiating surface, as may easily be seen from geometrical considerations. The rays which reach f must consequently proceed from e . Rays proceeding from any lower point of the surface will either be bent up so as never to reach the plate at all, or else they will strike it short of f . The ray which reaches f from e will clearly just graze the surface of the plate at f .

If r be the radius of curvature, b the distance ec , and l the distance cf , then—

$$h(2r - b) = l^2, \text{ or } r = \frac{1}{2} \left(\frac{l^2}{h} + h \right).$$

If then we measure b , the height of the highest part of the radiating surface above the plate, and l the greatest distance to which the darkening of the plate extends, we have data for determining r .

It must be admitted that the measurement of l involves great uncertainty. The image gradually tails off, and any estimate of its length must to a great extent be arbitrary.

The value of r deduced is more uncertain still, since l^2 is involved in calculating it. But, in spite of these objections, the method may, I think, be relied on to give the order of magnitude of r , and that is all that is required, so far as the conclusions which it is here sought to draw are concerned.

In one experiment the length l was estimated at 2 c.m.; b was 0.8 c.m. Thus $r = 3$ c.m. approximately.

The strength of the magnetic field, measured as before, was 1680 C.G.S. Thus the field required to produce a curvature of radius 1 c.m. is about 5×10^8 .

In another experiment, l was 1.8 c.m., b was 0.8 c.m., and the field 2140. This gives practically the same result as the preceding.

In an experiment described by Professor J. J. Thomson, a beam of cathode rays was bent to a radius of curvature of 9 c.m. in a field of 35 units. Thus a field of 315 would have been required to bend it to a radius of 1 c.m.

Let us now collect the results obtained, and compare them with this.

The field which would be required to produce a curvature of 1 c.m. radius would be—

For cathode rays	3×10^9
„ Becquerel rays	5×10^8
„ Röntgen rays not less than ..	6×10^7 .

If the Röntgen rays are magnetically deflected at all, it is by an amount less than a ten-thousandth part of that observed in the case of the Becquerel rays.

The magnetic deflectibility of the Becquerel rays cannot but be considered to be a most characteristic property. And the above result appears to make it tolerably certain that the Röntgen rays do not possess this property. It is to be concluded, therefore, that the Becquerel rays are, after all, essentially different in character from the Röntgen rays.

ON GADOLINIUM.*

By C. BENEDICKS.

(Continued from p. 53)

Identity of Gadolinium.

DOUBTS have been cast on the elementary character of gadolinium. Delafontaine imagined Marignac's Y_a to be a mixture of the terbium and decipium earths. This opinion was shown by Cleve, in 1885, to be untenable, since pure gadolinium earth is nearly colourless, whilst that of terbium earth is orange-coloured. As regards decipium earth, its identity with that of gadolinium might eventually be established, for the only differences pointed out by Delafontaine are the atomic weight 171 and the insolubility of the potassium double sulphate in saturated potassium sulphate solution. The reliability of the information concerning decipium earth is still questionable.

Sir W. Crookes, who himself prepared gadolinium earth from samarskite and made a searching study of its phosphorescent spectrum, concludes that three components are present in gadolinium. In consideration of the great delicacy of his method, and the less completely known relations which influence it, this should be recognised as a most valuable aid to the chemistry of the future, though, on the other hand, it scarcely promises great possibility of separation.

Demarçay's statement about an element coming next to samarium might, to a certain extent, be considered as a splitting up of gadolinium. For this hypothetical element, whose oxides and salts are to be colourless as should be those of gadolinium, would only be distinguishable from gadolinium by the greater solubility of the nitrate in concentrated nitric acid. The only foundation for belief in its existence is the spark spectrum. Demarçay has announced no atomic weight determinations of the different nitrate fractionations. In consequence, I have carried out determinations with material treated according to Demarçay's statements. These determinations only indicate that the atomic weight in the first fractions was slightly lower than in the last fraction II., with which the atomic weight determinations were made, the reason probably being that a small amount of samarium was still present in the first fractions.

By observation of the spark spectrum of fraction II., I could discover no E line. Still more conclusive evidence against the presence E_2O_3 in my material lies in the fact that it was re-crystallised ten times from concentrated nitric acid, by which means, according to Demarçay, E_2O_3 must have been removed. If it appears later that E_2O_3 is a fundamental substance of remaining elements, it is probable that it is absent in my material.

Spectrum.

The gadolinium spectrum has been studied and described by Lecoq de Boisbaudran. With reference to this, it appears that two eminent experimentalists, Thalen and Bettendorff, were unable to get a spectrum. The cause is to be found in the differences in the methods of procedure. Thalen used aluminium poles, covered with a chloride solution. By using a Salet tube in conjunction with an induction coil with a long secondary wire, one can obtain without difficulty a beautiful spectrum, which consists of bands and bright lines.

This spectrum, according to Lecoq, is specially beautiful when a Demarçay induction coil with a short secondary coil is used, the poles being placed as far apart as possible; with a short distance between the poles quite a different spectrum is obtained, consisting only of bright distinct lines.

Demarçay also announces a few Gd lines in the violet part of the spectrum.

There is no absorption band in the visible part of the gadolinium spectrum, but, according to Soret, there is an absorption band from λ 280 to λ 245 in the ultra violet.

Compounds of Gadolinium.

Gadolinium Oxide, Gd_2O_3 . the only oxide of this element, forms a white powder; a scarcely visible tinge in the yellow is probably caused by a minute trace of terbium oxide. It is easily soluble in acids; the reaction is slight at first, but on standing or through warming becomes very powerful. The oxide absorbs CO_2 quickly from the air, and is rather hygroscopic. The oxide is not reduced by heating in hydrogen, but, as Bettendorff has already discovered, a small quantity of a darker coloured earth is produced, which is somewhat less soluble in acids, but which has exactly the same atomic weight as the remaining earth, as determined by Bettendorff.

Specific gravity	I. 7.405 at 16°
"	II. 7.407 at 15°
Molecular volume	48.6.

Gadolinium hydroxide is a gelatinous precipitate, rapidly absorbing CO_2 from the air.

The salts of gadolinium are, with few exceptions, colourless; they have no absorption spectrum, and possess a sweet astringent taste. They resemble the salts of yttrium in these and in most other properties, as well as in their behaviour with regard to different reagents.

Gadolinium Chloride, $GdCl_3 + 6H_2O$.—Quadratic double pyramids, optically uniaxial, crystallising well in thick blunt plates. Crystallises from neutral solution over sulphuric acid in rather large, somewhat deliquescent crystals, and very easily from hydrochloric acid solution in smaller crystals, which contain the same quantity of water of crystallisation.

Analysis of $GdCl_3 \cdot 6H_2O$.

	I.	II.	III.	IV.
Gd ..	42.2	41.94	42.00	41.70 per cent.
Cl_3 ..	—	—	28.46	28.49 "
Calculated percentages	Gd	42.10 per cent.		
	Cl	28.75 "		
Mean specific gravity	2.424			
Molecular volume	152.8			

Gadolinium Bromide, $GdBr_3 + 6H_2O$.—Crystallises from the solution of the oxide in hydrobromic acid over sulphuric acid in small, pointed, rhombic plates, coloured brown by the presence of free bromine.

Analysis of Salt.

Gd ..	30.70 per cent.	Calculated 30.95 per cent.
Br_3 ..	—	" 47.62 "
Mean specific gravity	2.844	
Molecular volume	177.2	

Gadolinium Platinichloride, $GdCl_3 + PtCl_4 + 10H_2O$.—A quantity of this, together with some $GdCl_3$, crystallises from equivalent quantities of $GdCl_3$ and $PtCl_4$. Orange-yellow, prismatic needles. Fairly stable in air, but affording no measurement.

Analysis of Salt.

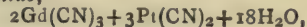
Gd ..	19.90 per cent.	Calculated 20.03 per cent.
Pt ..	25.0 "	" 25.01 "
Cl_4 ..	—	" 31.86 "
Specific gravity	2.719	
Molecular volume	286.5	

Gadolinium Aurochloride, $GdCl_3 + AuCl_3 + 10H_2O$.—Crystallises from the mixed solution of both salts ($AuCl_3$ in excess) in beautiful yellow plates after much concentration. The salt loses H_2O over sulphuric acid.

Analysis of Salt.

Gd ..	21.00 per cent.	Calculated 20.91 per cent.
Au ..	26.00 "	" 26.44 "
Cl_3 ..	—	" 28.52 "
Specific gravity	2.706	
Molecular volume	275.7	

Gadolinium Platinocyanide, —



was obtained by double decomposition of calculated quantities of gadolinium sulphate and barium platinocyanide and concentration of the filtered solution over sulphuric acid. Beautiful cherry-red rhombic crystals, some long and pointed, some tabular and flattened, which possess a bright metallic lustre on the prismatic and pyramidal surfaces. The salt is isomorphic with the corresponding yttrium and erbium compounds. As the angular differences between gadolinium on the one hand, and yttrium on the other, are very trifling, and the variations of individual measurements are often greater, I have not calculated the constant, as later in the case of other salts, but give only the corresponding angular measurements of the yttrium compounds, as they appear from the researches of Dr. H. Topsoë:—

	No. of crystals.	Edges.	Observed.	(Topsoë).
$110 : 110$	7	8	$83^\circ 27'$	$83^\circ 28'$
$110 : \bar{110}$	6	8	$96^\circ 27'$	$96^\circ 32'$
$001 : 110$	17	20	$88^\circ 24' - 91^\circ 40'$	$90^\circ 0'$
$\{ 001 : 221$	2	2	$61^\circ 44'$	$61^\circ 36'$
$\{ 110 : 221$	7	4	$28^\circ 36'$	$23^\circ 24'$

The optical orientation is the same as in the yttrium compound.

The crystals are not so stable in air as those of the yttrium and erbium compounds, but gradually decompose and become yellow.

Analysis of $2Gd(CN)_3 + 3Pt(CN)_2 + 18H_2O$.

Gd_2 ..	20.53 per cent.	Calculated 20.36 per cent.
Pt_3 ..	38.08 "	" 38.14 "
CN_{12} ..	—	" 20.36 "
$18H_2O$..	—	" 21.24 "
Specific gravity	2.563	
Molecular volume	597.9	

As already stated, this salt is isomorphous with the corresponding yttrium and erbium salts; the fine red colour and the green metallic lustre are common to all these compounds. The platino-cyanides of the cerium metals (to which samarium is allied) are, on the contrary, yellow with a blue metallic lustre, and crystallise in monoclinic prisms. Gadolinium therefore belongs to the yttrium group. But the water of crystallisation of the gadolinium compound is $18H_2O$, like that of cerium, whereas that of the yttrium and erbium salts is $21H_2O$.

(To be continued.)

A BIBLIOGRAPHY OF STEEL WORKS
ANALYSIS.

PART II.

TUNGSTEN AND MOLYBDENUM.

By HARRY BREARLEY.

(Continued from p. 50).

TUNGSTEN (*continued*).

II. GRAVIMETRIC ESTIMATIONS.

241. BERNOULLI (C. N., v., 116).—Fuse insoluble tungstates with soda carbonate; neutralise extract with acetic acid, precipitate with lead acetate, digest $PbWO_4$ in ammonium sulphide, evaporate filtrate with HNO_3 , and weigh WO_3 . By treating the nearly dried nitric solution with ammonia, niobic acid is left undissolved.
242. ZETTNOR (C. N., xvi., 12).—By precipitating with lead acetate from a faintly acetic acid solution (see 243).
243. BREARLEY (C. N., lxxix., 66).—The precipitate formed in acetic solutions with lead acetate is an indefinite acid tungstate of lead containing all the W. On dissolving in strong HCl and diluting, all the WO_3 is re-precipitated. $PbWO_4$ is soluble in alkaline acetates and chlorides, but not in nitrates. True $PbWO_4$ is formed in faintly ammoniacal solution, in presence of $(NH_4)NO_3$, by a few minutes' boiling.
- 243a. KERN (C. N., xxxv., 67).— WO_3 and SiO_2 separated from acid solution of iron, washed with HCl and alcohol. Separate SiO_2 with ammonia, and precipitate WO_3 from caustic filtrate with HCl.
244. PARRY and MORGAN (C. N., lxxvii., 260).—Acid solution of the steel is evaporated, but not baked. Filtered SiO_2 and WO_3 separated with ammonia (see 219).
245. KEMERY (J. I. S. I., 1894, i., 614).—Dissolve in nitro-sulphuric acid, evaporate to SO_3 fumes, separate SiO_2 with HF.
246. SCHNEIDER and LIPP (C. N., li., 297).—Steel attacked with Br and HNO_3 ; evaporated; residue not soluble in dilute HNO_3 fused and evaporated with HNO_3 ; SiO_2 and WO_3 separated with $KHSO_4$ and $(NH_4)_2CO_3$.
247. Vienna Assay Office (J. I. S. I., 1884, 230).—Decompose with aqua regia or bromine; separates SiO_2 as in 246.
248. PERILLOU (J. I. S. I., 1884, 629).—Dissolve in HNO_3 , evaporate, re-dissolve, boil two hours, weigh $WO_3 + SiO_2$, and heat to redness in dried HCl gas. The tungsten is volatilised (see 288); residual silica weighed.
249. SCHNEIDER (J. I. S. I., 1885, 245).—Iron alloys treated with HCl repeatedly. Only traces of tungsten pass into solution from alloys rich in tungsten.
250. NAMIAS (J. C. S., lxii., 539).—Rich alloys digested with Br in an alkaline solution and then evaporated with HCl. $WO_3 + SiO_2$ ignited in hydrogen (see 223); the loss in weight being calculated to WO_3 . Steel digested with HCl in absence of air; what little passes into solution is recovered by evaporating with sugar; charred residue contains $WO_3 + SiO_2$.
251. PREUSSER (C. N., lx., 37).—In rich alloys, powdered sample ignited to WO_3 , evaporated with acids, residue fused with soda carbonate, extract precipitated with HCl, SiO_2 separated with ammonia, $(NH_4)_2WO_4$ evaporated and ignited to WO_3 . Notes the solubility of SiO_2 in ammonia.
252. ZIEGLER (C. N., lx., 272).—Points out that tungsten attacks platinum, probably forming an alloy. Throws the W powder on to fused $(NH_4)NO_3$, which effects a superficial oxidation, and is volatilised.
253. WDOVISZEWSKI (J. I. S. I., 1895, ii., 597).—The FeW alloy fused with borax glass and NaK carbonates; water extract evaporated with HCl; washing with dilute $(NH_4)NO_3$ prevents WO_3 passing through the filter.
254. CREMER (J. S. C. I., 1895, 679).—Fuse the ore with pyrosulphate ($K_2S_2O_7$), dissolve in dilute HCl, add cinchonin, and wash WO_3 with cinchonin solution. Separate SiO_2 with ammonia.
255. ZIEGLER (J. I. S. I., 1890, i., 373).—Fuse with soda nitrate, evaporate extract with acid, separate SiO_2 and WO_3 with HF. Any W in the fusion residue is separated and precipitated with $HgNO_3$.
256. ZIEGLER (J. S. C. I., 1890, 216).—Behaviour of reagents with metallic W. Oxidation of a sample gauged by dusting into Na_2CO_3 kept fluid so that the W may sink promptly. Steel is attacked with nitro-sulphuric acid. A detailed account of the process 255 (see also J. S. C. I., 1891, 388).
257. HELMHACKER (J. S. C. I., 1896, 656).—Wolfram ore fused with soda carbonate; WO_3 precipitated from filtrate with acids; and SiO_2 and SnO_3 separated with HF and KCN fusions respectively.
258. CARNOT and GOUTAL (J. C. S., lxxii., 521).—Iron separated with copper solution. Residue freed from SiO_2 , fused, and precipitated with $HgNO_3$.
259. SCHÖFFEL (C. N., xli., 31; and J. I. S. I., 1880, 345).—Separate iron with solution of copper-ammonium chloride, and precipitate fused residue with $HgNO_3$. SiO_2 separated by fusion with $KHSO_4$. Roast alloys of over 12 per cent W, and fuse. Dissolve steels in aqua regia, dilute, and allow to stand one to two days.
260. VON DER FORDEN (C. N., l., 18).—Precipitation with $HgNO_3$ (Berzelius's method) or evaporation with HCl.
261. SMITH and BRADBURY (J. C. S., lxii., 241).—Tungsten may be estimated by means of its Ba, Pb, or Cd salts, but not effectually by means of the Sr, Ca, Ag, Co, or Bi salts.
262. LEFORT (C. N., xlv., 57).—To slightly acetic solution of a soluble tungstate add quinine acetate or sulphate. Destroy quinine by igniting and treating with HNO_3 . Method exact.
263. McKENNA (J. S. C. I., 1898, 1185).—FeW alloys decomposed with soda peroxide in Cu crucible; WO_3 precipitated by evaporation with HCl; Cr and Al are separated by $(NH_4)HO$. Carbon is determined by fusing with peroxide and estimating the carbonates formed.
264. PHILIPP (J. S. C. I., 1882, 152).—Powdered tungsten bronze heated with an ammoniacal solution precipitates Ag equivalent to the oxygen needed to completely oxidise the compound. The NaO and WO_3 are determined in the filtrate.
- 264a. IBBOTSON and BREARLEY (C. N., lxxx., 294).—Indirect process for estimating W in metallic powders depending on the solubility of the oxidised metal in NaHO. Results exact.

III. VOLUMETRIC ESTIMATIONS.

265. HUNDESHAGEN (J. C. S., lxxviii., 85).— WO_3 separated as usual, is dissolved in NaHO, and excess titrated.
266. HITCHCOCK (J. C. S., lxx., 526).—Uranyl nitrate or chloride precipitates W completely. A volumetric estimation, using ferrocyanide as indicator, is based on this fact. (See also 294).

IV. DETECTION AND MISCELLANEOUS NOTES.

267. MALLET (C. N., xxxi., 276).—A dilute HCl solution of an alkaline tungstate treated with sulphocyanate and some zinc assumes a fine amethyst colour. (See 300).

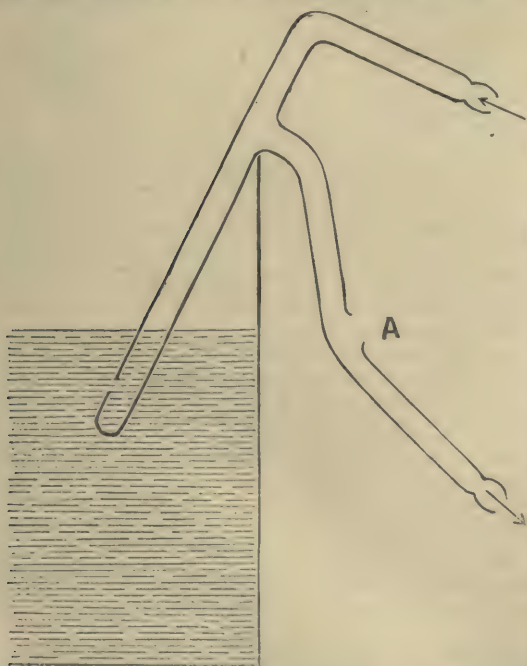
268. DEPAQZ (C. N., lxxiv., 88).—Zn or Al in an acidified solution of a tungstate gives blue colour. The material is got into solution with bisulphate and H_2SO_4 ; triturate with phenol (red colour) or hydroquinone (violet). Other organic reactions given.
269. LANGLEY (Y. I. S. I., 1893, i., 373).—By the use of an emery wheel, less than $\frac{1}{2}$ per cent W can be detected in steel; it gives only a dull fire instead of the brilliant showers of sparks.
270. SKEY (C. N., xiv., 256).— WO_3 suddenly refrigerated assumes a black colour permanent in air. Other new reactions.
271. SKEY (C. N., xvii., 157).—Recently ignited charcoal shaken up with a sulphuric solution of tungsten absorbs the W, but gives it up to caustic alkali.
272. CARNOT and GOUTAL (Y. C. S., lxxii., 555).— Fe_3W and Fe_3Mo_2 are left undissolved by dilute acids acting on iron; these bodies therefore exist in steel.
273. MOISSAN (Y. C. S., lx., 607).—Tungsten is readily dissolved by a mixture of HF and HNO_3 .
- 273a. BURGHARDT (C. N., lxi., 260).—Wolframite is decomposed by mixing with charcoal and projecting into fused soda. WO_3 precipitated from filtrate by making slightly acid with HCl. Chrome iron ore is similarly decomposed.
274. RIDDLE (Y. I. S. I., 1890, i., 365).—Powdered metallic tungsten in contact with concentrated HCl for three days was not at all dissolved.

(To be continued).

NEW FORM OF WATER-BATH REGULATOR.

By H. STAFFORD HATFIELD.

A SIMPLE device applicable to any vessel is often required for maintaining for some time without attention a constant level of liquid in a water-bath or similar apparatus. Some form of syphon is usually employed, connected with



a reservoir, maintained at constant level by inflow and outflow of water. But all such regulators cease to work in a short time if ordinary tap-water is used, because the heating of the inflowing water during its passage down

the syphon-tube fills the latter with air, and so the supply ceases, unless an air-collector of considerable capacity is sealed on at the highest point of the syphon.

The annexed figure illustrates a form of apparatus which renders unnecessary a reservoir, and which is not stopped in its action by air-bubbles. The supply-tube bifurcates, and one limb dips under the liquid in the bath. The other is opened to the air at A. The water in the bath will keep at the level of A, or slightly above it; the excess of level being due to the force necessary to divert the stream of water. All the tubes must be full of water, but air-bubbles on rising are immediately swept away by the current of water, which must be sufficient to do this properly, but need not be great. The water must leave the sides of the glass at A. The tubes may be bent to fit any particular form of vessel. After a thorough test, I am satisfied of its efficiency.

University College, London.

January 25, 1900.

THE ANALYSIS OF GLUE.

By R. WOY.

The methods now in vogue for the analysis of glue are those of R. Kissling (*Moniteur Scientifique*, March, 1899, p. 222).

According to Kissling, the proportion of fatty matters should vary from 0.001 to 0.09 per cent. Now, by making use of a method described by Hilger, very analogous to the so-called "gypsum" method for the extraction of alkaloids, the author found 0.24 to 0.67 per cent.

The sheets of glue are broken up in a covered mortar, into sufficiently small pieces, and 20 grms. are weighed out and placed in a porcelain crucible; to this are added 40–50 c.c. of boiling water, and 5–10 c.c. of hydrochloric acid to decompose the traces of soap which may be present in the substance. The glue is dissolved by gently heating with continuous stirring. A suitable quantity of gypsum is then added, a little at a time, until the mass becomes first pasty and then solid. The sides of the crucible are then scraped, and the whole dried for two to three hours at 105–110°.

The powder thus dried is placed in a small flask and exhausted with ether for five or six hours in a Soxhlet extractor. Finally, the ether extract is dried in an oven.

For the complete analysis of glue we dissolve 50 grms. of the sample by repeated treatments with water (200 c.c. at a time); the solution is made up to 1 litre and well mixed.

Estimation of the Water.—Evaporate 25 c.c. of the solution in a crucible, as in the estimation of the dry extract of wines, and dry the residue at 110° for three hours.

Ash.—The residue furnished by the estimation of the water is carbonised, the residue is moistened with alcohol and ground up, the alcohol is carefully driven off by heat and finally incinerated.

Nitrogen.—25 c.c. of the solution of glue are treated by Kjeldahl's method. To effect its decomposition the author used 20 c.c. of a mixture of three volumes of concentrated sulphuric acid, and two volumes of fuming sulphuric acid. To these 20 c.c. of acid there are added 10 grms. of anhydrous sulphate of potash and 2 grms. of anhydrous sulphate of copper.

Pure glue contains about 18.5 per cent of nitrogen.

Acidity.—100 or 200 c.c. of the solution of glue are diluted with water, and titrated with decinormal soda, using phenolphthalein as an indicator. We then add an excess of decinormal hydrochloric acid, and titrate again with soda. The acidity is expressed in c.c. of normal acid per 100 c.c. of glue.

Free Volatile Acids.—These are determined by distilling 20 to 30 grms. of glue in a current of steam, and titrating the distillate with normal soda.

Combined Volatile Acids.—These are estimated in the same manner, but sulphuric acid is added before distillation.

Sulphurous Acid.—Distil in a current of carbonic acid, collect the product of distillation in a solution of iodine, and precipitate with chloride of barium.

Finally, the author gives it as his opinion that, in the estimation of glues, chemical analysis is much to be preferred to mechanical tests, the results of which are always doubtful and liable to contradiction.—*Zeits. f. Offentl. Chem.*, iv., p. 755.

ON THE HEAT OF OXIDATION OF TUNGSTEN.

By M. DELÉPINE and L. A. HALLOPEAU.

WE decided to measure the heats of combustion of tungsten and of its lower oxide, WO_2 , for the purpose of comparing them with those of the other metals, and of assigning, in this respect, a place to tungsten in the series of the elements; the results obtained have led us to make certain experiments necessary to justify the position assigned to it by us.

Tungsten, W.—We only succeeded in obtaining satisfactory results after several failures. Combustion in oxygen at the ordinary pressure, combination with a halogen element, attack by water or by an acid, displacement by another element of which the heat of oxidation is known, &c., generally used for the determination of the heat of formation of an oxide, are not applicable to tungsten, or to its oxide, WO_2 , since tungsten does not burn in oxygen or chlorine unless it is heated continuously, and no other reactions into which it enters are sufficiently rapid; all these conditions are incompatible with the use of the calorimeter. It then occurred to us to make use of M. Berthelot's calorimetric bomb.

The finely divided tungsten (0.8 to 1.0 grm.) must be ignited by means of a little camphor (0.01 to 0.03 grm.), the camphor being set alight by a few grains of gun-cotton (0.01 grm. at the most), which is set fire to by means of a platinum wire brought to incandescence by means of an electric current. Thanks to this series of successive ignitions the spiral of iron wire, which might bring into the calculation the formation of an unknown quantity of tungstate of iron, is done away with.

It is also necessary to avoid the use of platinum; in our first experiment the tungsten burning in compressed oxygen (25 atmos.) pierced the crucible over a surface of several square c.m.s., the temperature being so high; possibly an alloy is formed.

Happily we placed a layer of water covered with a sheet of platinum at the bottom of the bomb; this sheet of platinum was also pierced, but the bomb was not injured. We were careful always to take the same precautions in our future experiments. Porcelain also cannot be used; it is always partially melted, and is even sometimes pierced. We finally decided to use the bottoms of clay crucibles of a uniform thickness, 6 to 7 m.m. in height and 10 to 15 m.m. in diameter.

Even then success did not always follow, but we were able to obtain sufficiently concordant figures in three experiments made with pure tungsten; that is, per grm., 1049, 1044, and 1093 cal., a mean of 1062 cal.

The first of these figures carries a slight correction, established by the determination in the product of combustion, the quantity of fresh oxygen capable of combination (0.0027 grm.); this brought the original figure from 1036 to 1049 cal.; in the two other experiments we were not able to fix any fresh oxygen.*

* If instead of burning pure tungsten we burn carburised tungsten, we obtain much higher figures; thus, a melted sample that we burnt gave off 1287 cal. per grm., which points to a proportion of 3 per cent of carbon present. In fact, on analysis this tungsten did not give the correct amount of tungstic anhydride.

Binoxide, WO_2 .—Our binoxide was a magnificently crystallised body. Its combustion offered none of the preceding difficulties; we were able to use a platinum crucible, and instead of operating at 25 atmospheres on 1 grm., we operated at 15 atmospheres, and even less, on 3 grms. of binoxide at a time. The combustion of each grm. of binoxide gave off: 292.8, 304.2, 293.1, 306.6 cal., or an average of 299.2 cal.

It results from these figures and from the preceding ones that—

$W + O_3 = WO_3 + 195.41$ cal. at constant volume + 196.3 cal. at constant pressure.

$WO_2 + O = WO_3 + 64.63$ cal. at constant volume + 64.9 cal. at constant pressure.

$W + O_2 = WO_2$ cal. at constant volume = 131.4 = 2×65.7 cal. at constant pressure.

The fixation of each atom of oxygen thus gives off nearly the same quantity of heat when combining with the metal or the oxide already formed; but if we are correct in regarding the heat of formation of WO_2 as exact to 1 cal., we are led to believe in too small a heat of oxidation for W into WO_3 .

Nevertheless, these results enable us to make a preliminary comparison with the heat of oxidation of a few bodies, with regard to the fixation of 1 atom of oxygen. The following table, which carries with it all the consequences mentioned later on, gives the amount of these heats of oxidation:—

	Cal.
Mg	143.4
Al	131.0
Alkaline and alkaline-earth metals >	90.0
Si	89.8
Zn	84.8
Sn	70.7
H(H_2O liq)	69.0
W	65.4
Fe into FeO	65.7
Fe into Fe_2O_3	65.2×3
Fe_3 into Fe_3O_4	67.7×4
$SK_2 + O_4$	60.2×4
H(H_2O gas)	58.3
Sb into Sb_2O_3	55.6×3
Pb	50.8
Cu into Cu_2O	43.8
Hg, Pb, Ag, Au	< 25.0

We know that aqueous vapour oxidises tungsten at a relatively low temperature, but that, inversely, hydrogen completely reduces tungstic anhydride at a high temperature, a result comparable with the action of H_2O and H on iron and its oxides, which tungsten resembles by its heat of oxidation and by the equality of the successive disengagements of heat in its different degrees of oxidation.*

We also know that tungsten does not decompose either silica, magnesia, or alumina; neither does it decompose the anhydrous oxides of the alkaline or alkaline-earth metals, as may be seen in the electrolytic preparation of the tungstates, when at a certain time they may be left in prolonged contact after the bath has become alkaline. On the other hand, magnesium gave with WO_3 a reaction of extreme violence. We did not think it worth while to try the action of the alkaline metals, but zinc gave a very important and perfectly regular reaction by which we were enabled to prepare tungsten.

The action of tin on the oxides themselves was not studied by us; but we found that, conformably with its great heat of oxidation, it brings the alkaline tungstates

* Water, as liquid, does not oxidise tungsten, but W and WO_3 decompose it with facility in the presence of alkalis without there being any reverse action following the formation of a dissolved tungstate—
 $W + 2KOH$ dis. + $2H_2O$ liq. = WO_2K_2 dis. + $3H_2$ + $(x - 1.9)$ cal.
 $WO_2 + 2KOH$ dis. = WO_2K_2 dis. + H_2 + $(x + 4.7)$ cal.
 [x = the heat of hydration of $4WO_3$ changed into metatungstic acid, $(WO_3)_4H_2O$.]

to the state of bronzes, and even separates metallic tungsten.

Inversely we found that tungsten easily decomposes the oxides of antimony, lead, and copper, and sets the metal of these oxides free, at the temperature of a simple gas-burner. It was therefore useless to examine the reduction of oxides, of which the formation gives off still less heat.

Tungsten changes the sulphates into sulphides, a result which conforms with the figures in the table.

Finally, its tendency to pass to the state of tungstic oxide may be made use of on the solutions of the last oxides in the table; the blue (W_2O_5) or red (WO_2) solutions contain the lower oxides of W, and reduce to the lower state of oxidation the cupric, mercuric, and platinum salts, and precipitate the metal in auric and argentic solutions; at the same time the blue or red colour disappears on account of the transformation to WO_3 .

The place assigned to tungsten according to the heat of oxidation, 3×65 cal. (about), seems to us to be amply justified by the preceding experiments.—*Bull. Soc. Chim.*, Series 3, xxi., No. 22.

ON THE COLOUR OF CARBIDE OF CALCIUM.

By HENRY MOISSAN.

WE have shown in previous papers, that the carbides of potassium, C_2K_2 , and of lithium, C_2Li_2 , can be prepared in the form of transparent colourless crystalline plates. We have also obtained carbide of aluminium, C_3Al_4 , in the form of well-crystallised transparent yellow plates. On the other hand, when we first prepared the carbides of calcium, strontium, and barium in the electric furnace, we described these new crystalline compounds as only being slightly transparent in very thin plates, and having a characteristic reddish brown appearance.

This reddish brown appearance and the colouration of the crystals are only due to an impurity. When carbide of calcium does not contain a trace of iron, it is quite transparent, like carbide of lithium or chloride of sodium.

We will give as examples the following experiments:—

1. When we heat metallic calcium to a dull red heat* in a crucible brasqued with pure amorphous carbon, obtained by the rapid decomposition of acetylene, we obtain a white carbide of calcium, decomposable by cold water, forming slaked lime, and giving off acetylene. The carbide, examined under the microscope, is found to consist of a mass of transparent crystals.

2. When we heat pure hydride of calcium, CaH_2 , of which we have described the preparation by the direct union of hydrogen and calcium (1 : 1) in a brasque of pure amorphous carbon, we obtain a white carbide of calcium, C_2Ca , in thin plates, which are quite transparent.

3. The result is identical when we repeat the previous experiment with crystallised nitride of calcium, N_2Ca_3 .

4. Acetylenic ammoniacal acetylide of calcium, $C_2Ca.C_2H_2.4NH_4$, which we obtained at 60° by the action of acetylene on calcium-ammonium, leaves, on its complete decomposition, a carbide of calcium, C_2Ca , of extreme whiteness, and which is quite transparent under the microscope.

Finally, we will give the following experiment:—We took this white carbide of calcium and mixed it with a quantity of oxide of iron; the whole was then melted in the electric furnace in a crucible of pure graphite. After cooling, we obtained a reddish brown carbide of calcium, exactly like the carbide prepared commercially.

Absolutely pure carbide of calcium is therefore trans-

* This synthesis of calcium carbide takes place at a low temperature; it can be done by heating a mixture of calcium and carbon in a porcelain crucible over a spirit flame. We must add, however, that the heat given off by the union of the carbon and the calcium is sufficiently great to bring about the fusion of the carbide of calcium—a fusion which has, up to the present, only been attained by means of the electric furnace.

parent; when it has a reddish brown appearance, this should be attributed to the presence of iron. A trace only of this metal is sufficient to produce the colouration.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 22.

ANTIMONIC ACIDS AND ANTIMONIATES.

By A. E. DELACROIX.

IN a preceding paper (*Journ. de Pharm. et de Chim.*, (6), vi., pp. 337 and 533), I proved the existence of two soluble antimonie acids. As they have nothing in common with pyro- and ortho-phosphoric acids, I propose calling them tetra-antimonic and tri-antimonic acids, names which are in accordance with the facts.

The first gives acid or monobasic salts $(Sb_2O_5)_4M_3O$, and neutral or bibasic salts $(Sb_2O_5)_3M_2O$.

The second gives monobasic salts $(Sb_2O_5)_3M_2O$, neutral or bibasic salts $(Sb_2O_5)_3(M_2O)_2$, tribasic salts $(Sb_2O_5)_3(M_2O)_3$, and other complex salts.

Tetra-antimonic Acid.—The crystallised hydrate of this body is prepared by completely freezing a solution of the acid. The ice is melted in alcohol, and thin flakes are collected, acting on polarised light. After desiccation in air, which takes place fairly rapidly, this hydrate is found to be $Sb_2O_5.4H_2O$. Found—water, 18.81; calculated—water, 18.36. Over sulphuric acid it becomes $Sb_2O_5.3H_2O$, and at 100° , $Sb_2O_5.2H_2O$. It answers to the amorphous hydrate of Daubrawa (*Bull. Soc. Chim.*, xxix., 118).

Tetra-antimonates.—The alkaline salts are soluble in water, but insoluble in water containing other salts. The bibasic salts are produced by the neutralisation of the acid by the alkaline bases. Alcohol precipitates them from this solution; this does not take place with the monobasic salts. After precipitation with alcohol, the precipitate is separated by rapid filtration, and set to dry on a porous plate. The acetates may be treated in the same manner, but a slight excess must be used. Thus prepared, these salts are amorphous. Crystallised salts, having the appearance of the hydrate described above, are obtained by freezing antimonie solutions to which suitable quantities of bases or salts of alkaline metals have been added. Desiccation makes them insoluble. The alkaline and alkaline-earth antimonates turn yellow on calcination, which appears to decompose them. The other tetra-antimonates are prepared from the acetates, of which it is better to use dilute solutions, to prevent the formation of compact masses which are difficult to wash. They are insoluble in water, soluble in concentrated HCl, more or less soluble in tetra-antimonic acid.

Certain tetra-antimonates split up, in the presence of water, into mono and bibasic triantimonates.

As the hydrate and tetra-antimonic acid both change easily into triantimonic compounds, it is necessary to make certain of the condition of the solutions used to make the tetra-antimonate. To effect this, the equivalent is taken in 1/10 normal soda of—(1) the last mentioned tetra-antimonic solution containing HCl; (2) of the same solution transformed into triantimonic acid; and (3) the weight per litre of Sb_2O_5 is determined; this may be done with sufficient accuracy by evaporating down a known volume, and weighing the calcined residue. It is easy to see that the difference of the two titrations $\times 3$ = the value of the tetra-antimonic acid of Sb_2O_5 , in solution in N/10 soda, on condition, of course, that this Sb_2O_5 was entirely in the tetra- state.

These data suffice for us to calculate in what proportion, the two antimonie acids existed in the original solution, and also how much hydrochloric acid was also present.

Bibasic Tetra-antimonate of Soda $(Sb_2O_5)_2Na_2O.9H_2O$.—This salt crystallises in flakes, and is prepared by freezing the acid exactly neutralised by soda. Found— Na_2O , 7.39; Sb_2O_5 , 73.42; H_2O and loss, 19.18.

Amorphous salt. Found— Na_2O , 7.51; Sb_2O_5 , 73.14; H_2O and loss, 19.35. Calculated— Na_2O , 7.18; Sb_2O_5 , 74.06; H_2O , 18.74. At 100° it loses $4\text{H}_2\text{O}$.

In aqueous solution this salt splits up according to the identical reaction that has been given to the decomposition of the tetra-vanadates, into meta and trivanadates.

Tetra-antimonic acid was neutralised (to phthalein) with $\text{N}/10$ soda. The solution, left to itself, became acid, and a tribasic salt, $\text{Sb}_2\text{O}_5 \cdot \text{Na}_2\text{O}$, crystallised out. After the lapse of some days, the reaction—

$$6(\text{Sb}_2\text{O}_5)_2\text{Na}_2\text{O} = 3(\text{Sb}_2\text{O}_5)_3\text{Na}_2\text{O} + 3(\text{Sb}_2\text{O}_5 \cdot \text{Na}_2\text{O}),$$
being complete, heat was applied to dissolve the tribasic salt. This salt neutralises a part of the monobasic salt, the neutralisation is completed with $\text{N}/10$ soda. The acidity thus measured is found to be equal to one-third of the acidity of the original tetra-antimonic acid. It is thus $2\text{Na}_2\text{O}$. The reaction which expresses this neutrality—
$$3(\text{Sb}_2\text{O}_5)_3\text{Na}_2\text{O} + 3(\text{Sb}_2\text{O}_5 \cdot \text{Na}_2\text{O}) + 2\text{Na}_2\text{O} = 4(\text{Sb}_2\text{O}_5)_3(\text{Na}_2\text{O}_2),$$

agrees with the decomposition into an acid, and a tribasic salt; on account of this decomposition the tetra-antimoniate should be prepared with great rapidity.

Monobasic Salt, $(\text{Sb}_2\text{O}_5)_4 \cdot \text{Na}_2\text{O}$.—This salt has not been isolated. The reaction, not very distinct it is true, of tetra-antimonic acid on methyl-orange points to the existence of acid salts. The monobasic salt appears to be produced by the action of salts of sodium with mineral acids, on tetra-antimonic acid, with which sulphate, nitrate, and chloride of sodium in excess give a precipitate. The clear liquid does not contain any antimony, and the titration of its acidity shows that $1\text{Sb}_2\text{O}_5$ has set at liberty $1/2\text{HCl}$. This can only be explained by the formation of a salt of the formula $(\text{Sb}_2\text{O}_5)_4\text{M}_2\text{O}$. The precipitate is decomposed by washing.

Mixed Salt, $(\text{Sb}_2\text{O}_5)_4\text{Na}_2\text{O} \cdot (\text{Sb}_2\text{O}_5)_2\text{Na}_2\text{O} \cdot 20\text{H}_2\text{O}$.—Products in the form of a crystalline powder, of which the composition is very similar to this, have been obtained by freezing: (1) A solution of $1\text{Sb}_2\text{O}_5$ and 3NaCl ; (2) a solution of $1\text{Sb}_2\text{O}_5$ and $1/2\text{NaOH}$. (1) Found— Na_2O , 5.93; Sb_2O_5 , 77.72; H_2O and loss, 16.35. (2) Found— Na_2O , 5.35; Sb_2O_5 , 78.52; H_2O and loss, 16.13. Calculated— Na_2O , 5.16; Sb_2O_5 , 79.86; H_2O , 14.97.

Bibasic Tetra-antimoniate of Potash, $(\text{Sb}_2\text{O}_5)_2\text{K}_2\text{O} \cdot 9\text{H}_2\text{O}$.—Crystalline salt, found— K_2O , 10.87; Sb_2O_5 , 70.42; H_2O and loss, 18.71. Amorphous salt, found— K_2O , 10.89; Sb_2O_5 , 71.48; H_2O and loss, 17.63. Calculated— K_2O , 10.53; Sb_2O_5 , 71.41; H_2O , 18.06. At 100° it loses $4\text{H}_2\text{O}$.

Bibasic Tetra-antimoniate of Baryta, $(\text{Sb}_2\text{O}_5)_2\text{BaO} \cdot 5\text{H}_2\text{O}$ (at 100°).—Found— BaO , 18.09; Sb_2O_5 , 71.32; H_2O and loss, 10.59. Calculated— BaO , 17.36; Sb_2O_5 , 72.45; H_2O , 10.19. It dissolves easily in concentrated HCl .

Monobasic Salt, $(\text{Sb}_2\text{O}_5)_4\text{BaO} \cdot 15\text{H}_2\text{O}$.—A crystalline powder obtained by freezing a solution of $1\text{Sb}_2\text{O}_5$ and 2BaCl_2 . Found— BaO , 8.42; Sb_2O_5 , 75.43; H_2O and loss, 16.15. Calculated— BaO , 9.00; Sb_2O_5 , 75.14; H_2O , 15.85. At 100° it loses $5\text{H}_2\text{O}$.

Action of Baryta on Tetra-antimonic Acid.—After several days contact of the two bodies in solution we obtain tribasic tri-antimoniate of baryta, $\text{Sb}_2\text{O}_5\text{BaO} \cdot 2\text{H}_2\text{O}$ (at 100°). Found— BaO , 29.35; Sb_2O_5 , 60.92; loss on calcining, 7.91. Calculated— BaO , 30.11; Sb_2O_5 , 62.82; H_2O , 7.07. This salt is slightly soluble in water, and easily so in HCl .

Bibasic Tetra-antimoniate of Copper, $(\text{Sb}_2\text{O}_5)_2\text{CuO} \cdot 9\text{H}_2\text{O}$.—Found— CuO , 9.12; Sb_2O_5 , 72.48; H_2O and loss, 18.40. Calculated— CuO , 9.03; Sb_2O_5 , 72.60; H_2O , 18.37. A green precipitate insoluble in water, soluble in tetra-antimonic acid. After several days contact with dilute potash it gives $\text{Sb}_2\text{O}_5\text{K}_2\text{O}$; the remaining precipitate, freed from the mother-liquor, is soluble in water. Tetra-antimoniate of copper dissolves slowly in ammonia, with which it forms an ammoniacal antimoniate, crystallising in hexagonal prisms.

Divers Tetra-antimonates.—The silver salt is easily soluble warm. The salt of cadmium and that of mercury do not dissolve until after several days contact with water, without doubt after having undergone the same transformation as tetra-antimoniate of soda.

The salts of nickel and cobalt give ammoniacal antimonates, blue for cobalt, red for nickel.

Triantimonic Acid.—For the preparation of this acid we used antimonic hydrate, well washed and dissolved hot.

The crystallised hydrate is prepared by the evaporation of the acid on the water-bath at 100° , or by spontaneous evaporation. That prepared by freezing, and dried in the air, is $\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$. Found— H_2O , 14.98. Calculated— H_2O , 14.44. Over sulphuric acid it becomes $\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. At 100° it loses very little water. This crystallised hydrate answers to Geuther's amorphous product (*Bull. Soc. Chim.*, [3], xvii., 207).

The amorphous hydrate is difficultly soluble in concentrated hydrochloric acid. Water separates the tetra-antimonic hydrate from this solution.

Triantimonates.—The preparation of the bibasic salts is analogous to that of the tetra-antimonates. The alkaline salts are soluble in water, the solutions being opaline. The bi- and tri-basic salts are precipitated by alcohol, the first in the amorphous state, the others separate slowly in the crystalline state. The monobasic salts do not act in the same manner.

The salts of the other metals are insoluble in water, and rather soluble in tri-antimonic acid.

The bibasic tri-antimonates are incompletely soluble in hydrochloric acid. They are distinguished from the tetra-antimonates, inasmuch as, when treated by the alkaline bases, in the presence of water, they do not give tribasic triantimonates, at least not at the ordinary temperature.

Bibasic Triantimoniate of Soda, $(\text{Sb}_2\text{O}_5)_3\text{Na}_2\text{O} \cdot 10\text{H}_2\text{O}$.—Amorphous salt found— Na_2O , 10.24; Sb_2O_5 , 75.16; H_2O and loss, 14.60. Crystalline salt found— Na_2O , 10.14; Sb_2O_5 , 75.37; H_2O and loss, 14.49. Calculated— Na_2O , 9.82; Sb_2O_5 , 75.94; H_2O , 14.21. At 100° it loses $3\text{H}_2\text{O}$.

Monobasic Triantimoniate of Soda, $(\text{Sb}_2\text{O}_5)_3\text{Na}_2\text{O} \cdot 11\text{H}_2\text{O}$.—The action of the salts of sodium with mineral acids on triantimonic acid is analogous to that of these reagents on the tetra acid.

With chloride of sodium $\frac{1}{2}\text{HCl}$ is set at liberty by $1\text{Sb}_2\text{O}_5$, and this is followed by the formation of an acid salt, $(\text{Sb}_2\text{O}_5)_3\text{Na}_2\text{O}$. Washing decomposes it. Freezing triantimonic acid, half neutralised by soda, gives a crystalline powder. Found— Na_2O , 5.15; Sb_2O_5 , 78.81; H_2O and loss, 16.04. Calculated— Na_2O , 5.09; Sb_2O_5 , 78.68; H_2O , 16.23. The action of triantimonic acid on methyl-orange, although not very distinct, also points to the formation of acid salts. To properly detect the end of the reaction requires very variable quantities of the bases, according to the alkali used.

To return to the yellow colour, only $\frac{1}{2}\text{LiOH}$ is required for $1\text{Sb}_2\text{O}_5$, while under the same conditions practically $\frac{1}{2}\text{NaOH}$ is required.

Bibasic Triantimoniate of Potash, $(\text{Sb}_2\text{O}_5)_3(\text{K}_2\text{O})_2 \cdot 10\text{H}_2\text{O}$.—The amorphous salt was prepared by precipitating with alcohol triantimonic acid treated with an excess of potash. Found— K_2O , 14.82; Sb_2O_5 , 71.87; H_2O , 13.14. Calculated— K_2O , 14.20; Sb_2O_5 , 72.26; H_2O , 13.54. Freezing gives only a mixture of the amorphous and crystallised salts. At 100° it loses $3\text{H}_2\text{O}$.

Bibasic Triantimoniate of Baryta, $(\text{Sb}_2\text{O}_5)_3\text{BaO} \cdot 5\text{H}_2\text{O}$ (at 100°).—A salt prepared by means of the acetate. Found— BaO , 22.72; Sb_2O_5 , 69.98; H_2O and loss, 7.30. Calculated— BaO , 22.61; Sb_2O_5 , 70.76; H_2O , 6.63. Insoluble in water, incompletely soluble in HCl , soluble in triantimonic acid.

9/10 Antimoniate of Baryta, $(\text{Sb}_2\text{O}_5)_{10}(\text{BaO})_9 \cdot 18\text{H}_2\text{O}$.—This salt results from the prolonged action of baryta water on the acid. Found— BaO , 28.62; Sb_2O_5 , 64.81; H_2O and loss, 6.57. Calculated— BaO , 28.14; Sb_2O_5 , 65.24; H_2O , 6.61. Besides its different composition this salt is

distinguished from the tribasic triantimoniate by its insolubility in HCl.

Bibasic Triantimoniate of Copper, $(\text{Sb}_2\text{O}_5)_3(\text{CuO})_{10}\text{H}_2\text{O}$.—Found— CuO , 12.22; Sb_2O_5 , 73.61; H_2O and loss, 14.17. Calculated— CuO , 12.25; Sb_2O_5 , 73.89; H_2O , 13.86. When heated to dull redness it becomes almost black; at a higher temperature it decomposes with transient incandescence and emission of white antimonial fumes. It is insoluble in water, and soluble in triantimonic acid. Slightly soluble in NH_3 , while the tribasic salt dissolves, giving a crystallised ammoniacal antimoniate of copper.

Bi-acid Triantimoniate of Copper, $(\text{Sb}_2\text{O}_5)_6\text{CuO}, 16\text{H}_2\text{O}$.—This salt was prepared by exactly precipitating triantimonic acid by acetate of copper. Found— CuO , 3.11; Sb_2O_5 , 84.10; H_2O and loss, 12.79. Calculated— CuO , 3.48; Sb_2O_5 , 83.92; H_2O , 12.59. With dilute potash it gives a decided opaline solution.

I propose completing this research by the description of those antimonates which have as yet only been mentioned, and of others I have prepared.

M. Sanderens, not noticing my previous research, claims to have obtained a new antimononic acid (*Bull. Soc. Chim.*, [3], xxi., p. 53). Such cannot be the case, for the solutions made, according to his description, must contain tri- and tetra-antimonic acids. This important fact has been overlooked by him.

As to the salts formed by these acids, we do not agree with regard to their composition. M. Sanderens attributes to them the general formula $\text{Sb}_2\text{O}_5\text{M}_2\text{O}$, which is different to the results described above.—*Bull. Soc. Chim.*, Series 3, xxi., No. 24.

NOTICES OF BOOKS.

A Text-book of Physiological Chemistry. By OLOF HAMMERSTEN. Authorised Translation from the Author's Enlarged and Revised Fourth German Edition, by JOHN A. MANDEL. Third [American] Edition. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1900. Pp. 628, 8vo. Ill. Cloth.

THE second American edition of this standard work was reviewed in the CHEMICAL NEWS, January 13th, 1899, and it is only necessary to add here that Professor Mandel, desirous of keeping his work up to date, has incorporated new matter from the fourth German edition.

Dr. Hammersten says in his Preface that this work does not claim to be a complete handbook, but only a concise text-book, and he has succeeded in condensing some portions by re-writing, so that this edition occupies fewer pages than the former.

The reviewer is reminded of Professor A. W. von Hofmann's "Einleitung in die Moderne Chemie," which bears on the title-page of the fifth edition the unusual words "*gekürzte und verbesserte Auflage*," thus recognising the important fact that condensation is compatible with improvement and brevity with excellence.

The Index to this book fills sixty-two columns.

Führer durch die gesammte Calciumcarbid- und Acetylen-Literatur. Bibliographie der auf diesen Gebieten bisher erschienenen Bücher, Journale, Aufsätze in Zeitschriften, Abhandlungen und wichtigeren Patentschriften, unter Mitwirkung von A[nton] Ludwig, herausgegeben von S. Calvary & Co. Berlin. 1899. 8vo. Pp. 51.

THIS Guide to the Literature of Calcium Carbide and of Acetylene contains nearly 1000 titles of books, pamphlets, and articles in periodicals relating to these subjects. The arrangement is alphabetical by authors, the typography is clear, and the matter shows care in editing. It includes the literature of apparatus, and cites papers in forty-six

books and journals: it also refers to the more important American, German, British, and French patents. The bibliography was suggested by the Second International Acetylene Exhibition held at Budapest, and special attention is given to the technical side of the subject.

It is of interest to compare Dr. Ludwig's booklet with one published by the Smithsonian Institution in 1898—"Review and Bibliography of the Metallic Carbides," by J. A. Mathews. The two do not cover the same ground, but overlap in the section of calcium carbide: Dr. Ludwig treats of the industrial manufacture and applications of acetylene, Mr. Mathews of the metallic carbides in general regarded as chemical compounds; their treatment of the subject differs, yet each has its own peculiar advantages as well as its weaknesses. Mr. Mathews gives the dates of the journal-articles, Dr. Ludwig unfortunately omits them. On the other hand, the American omits initials of authors, and the German properly retains them; the former groups the references under specific headings, the latter adheres to the alphabetical plan; the German work has a commercial aspect, the American a purely scientific one. The two supplement each other. Those interested in acetylene would do well to secure both these pamphlets, which are sold at nominal prices, and further search in literature will probably become unnecessary.

H. C. B.

A Course of Practical Chemistry. By M. M. PATTISON MUIR, M.A. Part II. Intermediate. London: Longmans, Green, and Co. 1899. Pp. 234.

IN this, the second part of "A Course of Practical Chemistry," the author has adhered to the plan adopted in the first part, viz., to give a course of laboratory work which will help to train the student in the methods of chemical inquiry.

The student has already gone through the experiments showing the principles of qualitative analysis in Part I.; the present volume deals principally with more advanced and complex qualitative analysis, and the ground work of quantitative analysis.

The book comprises five sections, dealing respectively with: I. Volumetric or titrimetric analysis. II. Preparation of certain compounds, and examination of some of their reactions. This section includes the preparation of a number of chromium compounds, and experiments with nitric acid. III. Qualitative analysis of moderately complex mixtures of salts, also of metals and alloys, besides a number of appendices on the qualitative work. IV. The determination of some equivalent weights and some molecular weights. V. On gravimetric analysis. There are a few illustrations, but most of them could easily be dispensed with; students who have already gone through one year's course of practical chemistry, do not need an illustration of a wash-bottle, a bulb at the end of a glass-tube, how to pour a liquid into a filter, &c.

The book closes with a collection of tables, and a note on the application of the electrolytical ionisation theory to analytical reactions.

Artificial Perfumes ("Les Parfums Artificiels"). By EUGENE CHARABOT, Professor of Chemical Analysis at the Commercial Institute of Paris. With 25 Figures in the Text. Paris: J. B. Baillière and Son. 1899. Pp. 296.

OF late years there has been a large amount of work done on perfumes; papers, often contradictory, have accumulated with extraordinary rapidity, while commercial competition has become more and more keen. It is therefore not without difficulty that M. Charabot has succeeded in picking out the most salient points, and discerning, among the many opinions expressed, which are the best substantiated by facts.

The present volume will be of great use to chemists

and others who are interested in the subject of preparing perfumes of a definite composition. Those products which are of the greatest interest from the point of view of their application are torpeneol, vanilla, piperonal or heliotropine, ionone or artificial violet, and artificial musk. The author has also devoted a good deal of attention to several natural principles of definite composition, such as linalol, borneol, safral, &c., which, though not directly used in the perfumery industry, serve as primary materials for the subsequent preparation of artificial perfumes.

The author is to be congratulated on having produced a useful practical work, and also on the table of contents and index, both of which appear to be very complete.

CORRESPONDENCE.

LAW OF ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—Nobody has so powerfully claimed the attention of the scientific world to the mathematical laws of the atomic weights as you, Sir.

I will present you, therefore, the law that I have discovered and demonstrated to the Society of Naturalists in Warsaw the 15/27 January, 1900, as follows:—

I. The atomic weights disposed in a series from He to Na present the property that the sum of the members equidistant from the ends of the series is constant:—

$$\begin{aligned}\text{He} + \text{F} &= 4 + 19 = 23 = \text{Na} \\ \text{Li} + \text{O} &= 7 + 16 = 23 = \text{Na} \\ \text{Be} + \text{N} &= 9 + 14 = 23 = \text{Na} \\ \text{B} + \text{C} &= 11 + 12 = 23 = \text{Na}\end{aligned}$$

II. The same law governs, approximately, the series of elements from He to K:—

$$\begin{aligned}\text{He} + \text{Cl} &= 4 + 35.45 = 39.45 = \text{K} + 0.34 \\ \text{Li} + \text{S} &= 7.03 + 32.07 = 39.10 = \text{K} - 0.01 \\ \text{Be} + \text{P} &= 9.08 + 31.02 = 40.10 = \text{K} + 0.90 \\ \text{B} + \text{Si} &= 10.95 + 28.40 = 39.35 = \text{K} + 0.24 \\ \text{C} + \text{Al} &= 12.01 + 27.11 = 39.12 = \text{K} + 0.01 \\ \text{N} + \text{Mg} &= 14.04 + 24.28 = 38.32 = \text{K} - 0.79 \\ \text{O} + \text{Na} &= 16 + 23.05 = 39.05 = \text{K} - 0.06 \\ \text{P} + \text{Ne} &= 19.06 + 20.05 = 39.11 = \text{K}\end{aligned}$$

III. The same law governs, approximately, the series of elements from He to Cu:—

$$\begin{aligned}\text{He} + \text{Co} &= 4 + 58.93 = 62.93 = \text{Cu} - 0.67 \\ \text{Li} + \text{Ni} &= 7.03 + 58.69 = 65.72 = \text{Cu} + 2.12^* \\ \text{Li} + \text{Fe} &= 7.03 + 56.02 = 63.04 = \text{Cu} - 0.36 \\ \text{Be} + \text{Mn} &= 9.08 + 54.99 = 64.07 = \text{Cu} + 0.47 \\ \text{C} + \text{V} &= 12.01 + 51.38 = 63.39 = \text{Cu} - 0.31 \\ \text{Ni} + \text{Ti} &= 14.04 + 48.15 = 62.19 = \text{Cu} - 1.41^{\dagger} \\ \text{O} + \text{Ti} &= 16 + 48.15 = 64.15 = \text{Cu} + 0.55 \\ \text{F} + \text{Sc} &= 19.06 + 44.12 = 63.18 = \text{Cu} - 0.42 \\ \text{Na} + \text{Ca} &= 23.05 + 40.07 = 63.12 = \text{Cu} - 0.48 \\ \text{Mg} + \text{K} &= 24.28 + 39.11 = 63.39 = \text{Cu} - 0.21 \\ \text{Al} + \text{Ar} &= ? \\ \text{Si} + \text{Cl} &= 28.40 + 35.45 = 63.85 = \text{Cu} + 0.25 \\ \text{P} + \text{S} &= 31.02 + 32.07 = 63.09 = \text{Cu} - 0.51\end{aligned}$$

* Exception; due to triad Co, Ni, Fe.

† Exception.

I cannot attempt any experiments suggested by this law, because I am a mathematician, not a chemist.—I am, &c.,

Prof. Dr. N. DELAUNAY.

Russia, Varsovie,
Institut Polytechnique de l'Empereur Nicolas II.,
16/28 January, 1900.

LABORATORY LAMP.

To the Editor of the Chemical News.

SIR,—In reply to "Chemicus," I would recommend him to invest in a benzene lamp (to be obtained of Gustave Barthel, Leipzig, for about 16 shillings).

They deserve to be better known. A very high temperature is easily obtained and controlled (1 grm. coal, in a platinum crucible, can be burnt, in order to estimate the ash, in fifteen minutes). The lamp is easily kept in order, is quite safe to use, and my experience with it and the methylated spirit lamp is decidedly in favour of the former. —I am, &c.,

RUDOLF E. WEISSMÜLLER.

Lukavac, Bosnia, January 22, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 3, January 15, 1900.

Numerical Laws of Chemical Equilibrium.—O. Boudouard.—There ought to exist a relation between the different factors of equilibrium (temperature, electromotive force, pressure, physical state, chemical nature, condensation, or concentration). This relation is such that each of the factors is a function, and a continuous function, of the others. This is known exactly in the law which concerns the correlative changes of pressure and temperature (Clapeyron's formula). There exists, further, at constant pressure and temperature, a certain relation between the proportions of different bodies present in a gaseous mixture in equilibrium (Isambert's experiments on ammonium sulphhydrate). If L is the heat of the reaction at constant pressure; T , the absolute temperature; P , the total pressure of the mixture; CC' . . . C_1C_2' , the concentrations of each of the bodies entering into the reaction; nn' . . . n_1n_2' , the number of molecules of each of the bodies concerned in the reaction; N , the algebraical sum of $n+n'$. . . $-n_1-n_2'$; the author arrives at the expression—

$$500 \int \frac{dT}{T^2} + N \log_e P + \log \frac{C^n C^{n'}}{C_1 n_1 C_2 n_2'} = \text{constant.}$$

The concordance of numbers found by this formula is satisfactory.

Electrolysis of Potassium Chloride.—A. Brochet.—Several theories have been brought forward to explain the presence of hypochlorites and chlorates after electrolysis of the chlorides of the alkalis and alkaline earths. The author studies the case of the electrolysis of a solution of sodium chloride, but he suppresses the reduction by the addition of a small quantity of potassium bichromate—a proceeding adopted by Muller. The results are shown on a curve. In the presence of potassium chromate, at a temperature of 20°, in a scarcely alkaline or neutral liquor, chlorate is formed, with a yield of 70 per cent. Without chromate, as Foerster has shown, the chlorate never exceeds 35 per cent; but it must be remembered that, in this latter case, half the quantity of electricity is employed in reducing the hypochlorite.

A New Crystalline Molybdenum Sulphide.—Marcel Guichard.—The author obtained, by the action of a very high temperature on molybdenum bisulphide, a crystalline sesquisulphide. This new sulphide can, at a red heat in sulphur vapour, be re-converted into the bisulphide. It is known that the bisulphide can otherwise be obtained by the action of a temperature below red heat

on the trisulphide. The bisulphide is the most stable in the neighbourhood of red heat. The sesquisulphide dissociates at a temperature approaching that at which it is formed, and yields metallic molybdenum. There is no molybdenum sulphide stable at a very high temperature. By starting with the trisulphide, MoS_3 , we can obtain by successive dissociations at higher and higher temperatures, first the bisulphide (MoS_2), then the sesquisulphide (Mo_2S_3), and finally the metal.

Action of Magnesium on Saline Solutions.—Henri Mouraour.—The author continues his research on this subject, and finds that it is not only with the solutions previously examined that magnesium acts more vigorously than with water, but also with solutions of perfectly different salts, and especially with ammoniacal salts. It is probable that these solutions (chiefly the ammonium salts) act by dissolving the magnesia which, forming on the surface of the magnesium, would tend to arrest the action.

Journal de Pharmacie et de Chimie,
Series 6, Vol. x., No. 9.

Analysis and Titration of Cacodylates.—H. Imbert and A. Astruc.—One of the authors has shown that

cacodylic acid, $\text{AsO} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{CH}_3 \end{smallmatrix}$, behaves as a neutral body to

heliantine, and is monobasic to phenolphthalein; this leads to a very simple method of estimating this body. Since cacodylate of soda is theoretically neutral to phenolphthalein, and, on the other hand, cacodylic acid is neutral to heliantine, it appeared probable that the quantity of a monobasic acid, such as HCl, necessary to add to a sodic salt to make it neutral to heliantine, ought to be exactly one molecule of acid for one molecule of the salt, according to the equation

$\text{AsO} \begin{smallmatrix} \text{ONa} \\ \diagup \\ \text{CH}_3 \end{smallmatrix} + \text{RH} = \text{AsO} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{CH}_3 \end{smallmatrix} + \text{RNa}$. By applying this

reaction to several commercial samples, we obtained the following results:—

	I.	II.	III.
Quantity of pure dry cacodylate of soda, per cent	92.80	88.00	75.20

Neither of these samples was neutral to phthalein, but all had a distinct acidity. The most convenient method of working is the following:—Dissolve 1.6 grms. of cacodylate of soda in 100 c.c. of distilled water; 10 c.c. of this solution are taken, and made neutral to phenolphthalein. The solution, to which is added a few drops of heliantine, is then titrated with a solution of hydrochloric acid at 3.65 grms. per 1000, or sulphuric acid at 4.9 grms. per 1000. This solution is added with a graduated burette until methyl-orange indicates the termination of the reaction. If n is the number of c.c. of acid solution used, the sample under examination contains $n \times 10$ per cent of pure cacodylate of soda.

A New Method for the Gravimetric Estimation of Reducing Sugars.—Dr. Ph. Chapelle.—This method is based on the action of the centrifugal machine, which is now coming into more common use in laboratories; it is driven by water pressure from the main, and makes about 3000 revolutions per minute. 100 c.c. of Fehling's solution, containing 1 gm. of cuprous oxide, is used, and 25 c.c. of this solution is mixed with the sugar solution, and the volume made up to 37.5 c.c. The tube is heated in a bath of a solution of chloride of lime boiling at about 110° for six minutes in the case of glucose, and ten minutes for lactose. It is then put in the centrifugal machine. After two or three minutes, the precipitate adheres so strongly to the sides of the tube that the latter can be turned upside down and drained on linen. The deposit is taken up with boiling distilled water, and the tubes again submitted to centrifugal force, decanted, and dried at 150 – 180° . The whole operation does not take more than twenty-five to thirty minutes.

Analysis of the Gum of the "Grevillea robusta."—MM. Roeser and Puaux.—This gum is exuded on the branches and trunk of the tree; it has no smell, but an astringent taste. Dried at 100° , it takes an odour of caramel and becomes very friable. Its aqueous solution is colourless and limpid, or perhaps slightly clouded; it is neutral to litmus. It is easily precipitated by alcohol at 95° ; it is also precipitated by the basic acetate of lead after the solution has been made slightly alkaline with ammonia. It reduces a cupro-potassic solution very slightly. It is not acted upon by silicate of potash, stannous chloride, or mercurous nitrate. When treated with mineral acids, this gum gives galactose and pentaglucoase (arabinose); the quantity of the former being slightly in excess of that of the latter.

No. 10.

This number contains no matter of chemical interest.

No. 11.

New Process for the Titration of Iodide of Potassium.—E. Vincent.—The process devised by the author is based on the same principles as that of M. Berthet. It consists of reacting with iodic acid on iodine as follows:— $6\text{HIO}_3 + 5\text{KI} = 5\text{KIO}_3 + 3\text{I}_2 + 3\text{H}_2\text{O}$. The five-sixths of iodine set free comes from the iodide; it is estimated by titration with hyposulphite of soda. One gm. of the iodide is dissolved in 1 litre of distilled water, and 2 grms. of iodic acid are dissolved in another litre of water. By means of a pipette, take 100 c.c. of each of these solutions and mix them together; measure 5 or 10 c.c. of hyposulphite solution containing 2.48 grms. per cent and containing 2 grms. of bicarbonate of potash per litre; run the iodine solution, drop by drop, from a burette into the hyposulphite solution until a faint yellow colour appears. This process is simple and rapid, and gives good results.

The Bubonic Plague.—M. Grimbart.—The bacillus of bubonic plague was discovered by Yersin in 1894, during the epidemic at Hong Kong. The disease occurs in four forms:—(1) Bubonic, (2) septicemic, (3) pneumonic, and (4) ambulatory; the latter form, which is very mild and sometimes overlooked, only occurs where the plague is endemic. The bacilli are met with in the blood, in ganglia, in phylacteria, and in the pneumonic phlegm. The cocco bacillus of plague is non-motile, and forms chains when cultivated in broth; it does not liquefy gelatin, and does not give any characteristic culture on potatoes; it is aerobic, does not form spores, and is killed at a temperature of 50° ; it produces a slightly diffusible toxin. It is of interest to note that the plague can be given to monkeys by inoculation, or through the trachea or nose, but never through the digestive organs.

MISCELLANEOUS

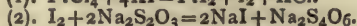
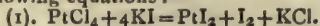
Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The Hon. Evelyn Ellis, the Hon. Everard Feilding, the Hon. Francis Robert Henley, Mr. C. E. Newton, and Mr. R. Oliver were elected members. The special thanks of the Members were returned to Mr. Charles Hawksley for his donation of £100, to Mr. Frank McClean for his donation of £25, and to Sir Andrew Noble, K.C.B., for his donation of £100 to the fund for the Promotion of Experimental Research at Low Temperatures. The Chairman reported the decease of Professor David Edward Hughes, F.R.S., a Manager of the Royal Institution, on January 22 last. The following resolution was submitted:—“Resolved,—That the Managers desire to express to Mrs. Hughes their heartfelt sympathy in her sad bereavement, and the deep regret of the Managers in losing by the death of Professor Hughes a most valued colleague.” Professor Hughes

became a Member of the Royal Institution in 1882. He delivered a discourse on "Theory of Magnetism" (illustrated by experiments), on February 8, 1884. As a Manager and Vice-President he has rendered important services to the Institution. And his scientific researches, which have received world-wide recognition, have done much to promote the objects of the Institution.

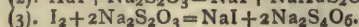
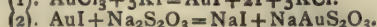
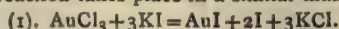
Analysis of Sulphide of Antimony.—M. Kitzing.—**1. Total Sulphur.**—0.9 gm. of the sample, previously dried at 105–110°, is mixed with 5 grms. of tartaric acid, and dilute nitric acid added drop by drop; it is then concentrated until all action ceases. After standing for twenty-four hours a few c.c. of bromine are added, when it is again allowed to stand for a night; a few crystals of iodine are then added to facilitate the solution of the last traces of sulphur. The excess of bromine is driven off by heating on the water-bath and frequently adding water: it is then evaporated several times with hydrochloric acid to drive off the nitric acid. The residue is taken up with hydrochloric acid and tartaric acid diluted with boiling-water. After filtration the sulphur is precipitated with chloride of barium. **2. Free Sulphur.**—Stibnite sometimes contains as much as 20 per cent of free sulphur. For the purpose of estimation, 10 grms. of the dry sample are exhausted with ether in a Soxhlet extractor. The exhaustion should last thirty hours. **3. Antimony.**—0.2 gm. of the substance are dissolved as in 1, and filtered; the antimony is then precipitated with sulphuretted hydrogen. The precipitate is oxidised with fuming nitric acid, and the oxide of antimony, SbO₂, weighed. **4. Water.**—Dry at 105–110° until the weight is constant. **5. Matter Soluble in Water.**—Digest a few grms. of the sample in warm water on the water-bath; filter and evaporate the solution in a tared platinum crucible.—*Zeits. fur Offentl. Chem.*, iv., p. 830.

Titrimetric Estimation of Bismuth by Arsenious Acid in Alkaline Solution.—C. Reichard.—The process devised by the author depends on the reduction of bismuthic acid by arsenious acid in alkaline solution, and the estimation of the unused arsenious acid. The compound of bismuth is dissolved in an acid, and an excess of alkali is added to the solution thus obtained. After heating, a current of chlorine is passed through. The solution is boiled until the precipitate formed changes from an orange-red to an intensely deep red colour. The bismuthic acid is well washed with water. A solution of arsenious acid in caustic soda is then added, the solution containing 0.01 gm. As₂O₃ per c.c. The whole is then boiled until the red bismuthic acid is transformed into white hydroxide. It is then acidulated strongly with sulphuric acid and filtered hot. The arsenious acid which has not taken part in the reaction is estimated in the clear filtrate, by means of permanganate. It is advisable only to take small samples of bismuth.—*Zeit. Anal. Chem.*, 1899, xxxviii., p. 100.

Volumetric Estimation of Gold and Platinum.—Heinrich Petersen.—The method devised by the author is based on the following facts:—When we pour a solution of platonic chloride into a sufficiently concentrated and cold solution of potassium iodide, iodine is set at liberty, the amount of which can be estimated by means of hyposulphite of soda. The reaction takes place according to the following equations:—



From this it results that 1 atom of platinum (194) is indicated by 2 molecules of sodic hyposulphite (316). With gold the reaction takes place in a similar manner:—



3 molecules of Na₂S₂O₃ take part in the reaction, and it is only after the formation of the double salt NaAuS₂O₃ that the hyposulphite acts on the free iodine.—*Zeit. Anorg. Chem.*, 1899, xix., p. 59.

MEETINGS FOR THE WEEK.

- MONDAY, 12th.**—Society of Arts, 8. (Cantor Lectures). "The Nature and Yield of Metalliferous Deposits," by Bennett H. Brough.
- TUESDAY, 13th.**—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
- WEDNESDAY, 14th.**—Society of Arts, 8. "The Diffraction Process of Colour Photography," by Prof. R. W. Wood. Institution of Mining and Metallurgy, 8. "The Gold-bearing Alluvial Deposits of the Klondyke District," by J. B. Tyrrell, F.G.S.
- THURSDAY, 15th.**—Royal Institution, 3. "Modern Astronomy," by Prof. H. H. Turner, M.A., F.R.S. Chemical, 8. "Ammonium Amidodisulphite" and "Products of Heating Ammonium Sulphites, Thiosulphates, and Trithionates," by Edward Divers and Masataka Ogawa. "Note on the Refraction and Magnetic Rotation of Hexamethylene," by S. Young, D.Sc., F.R.S., and Emily C. Fortey, B.Sc. "The Combination of Sulphur Dioxide and Oxygen," by Edward J. Russell and Norman Smith. "Note on the Estimation of Gases containing Sulphur," by E. J. Russell. "Apiin and Apigenin—II. Note on Vitexin" and "The Yellow Coloring Principles of Various Tannin Matters—VII," by A. G. Perkin.
- FRIDAY, 16th.**—Royal Institution, 9. "Life in Indo-China," by H. Warington Smith, M.A., LL.M., F.R.G.S.
- SATURDAY, 17th.**—Royal Institution, 3. "The Idea of Tragedy in Ancient and in Modern Drama," by W. L. Courtney, M.A., LL.D.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2099.

ON THE USE OF ICELAND SPAR AS A STANDARD IN VOLUMETRIC ANALYSIS.*

By ORME MASSON, M.A., D.Sc.

Introductory.

IN all volumetric work the first requisite is some substance of such a character that an exactly ascertained weight of it has a perfectly definite value in relation to the work in hand, whether this be alkalimetry, chlorine estimation, or what not. The strength of all the solutions employed is found by direct or indirect reference to this standard, and its selection is therefore a matter of fundamental importance. The substance employed must be readily obtainable in the required state; either chemically pure, in which case its value is calculable from its formula; or in pure aqueous solution, so that its value can be found by the measurement of a single physical property, such as density, or by the gravimetric estimation of a single chemical constituent. Where purity, either complete or partial is assumed, there should be no room for doubt as to the truth of the assumption. Where physical measurements or chemical estimations are necessary, the processes involved should be as simple as possible, not merely to save time and trouble, but more especially to minimise error. And, in any case, the standard substance should have no tendency to alter its composition on exposure to the air, as such a tendency renders troublesome precautions necessary, and even these do not always prevent error.

Few, if any, of the standards used in acidimetric and alkalimetric work approach the ideal. Oxalic acid is now generally condemned because of its variability in respect to hydration. The gravimetric analysis of solutions of hydrochloric or sulphuric acid by ordinary precipitation methods is not in much favour, nor is any process likely to be so which involves filtration, washing, and incineration. The analysis of sulphuric acid solution by converting it into the ammonium salt has been recommended, and is doubtless capable, like other methods, of giving correct results under certain conditions; but it is a serious objection that the salt to be weighed must be first obtained by evaporation, and then completely dried below 60° C. The fixing of the value of a sulphuric acid solution by determination of its density involves, in the first place, the assumption that the solution is as free from impurities as that employed by the investigator whose density tables are relied on, and, in the second place, it depends on a physical measurement which, without special precautions, cannot be trusted to give very accurate results. The only standard alkali in general use is sodium carbonate, which is made as required by heating a suitable quantity of pure bicarbonate. This method also fails of perfection; first, because the bicarbonate is liable to contain impurities (chlorides, sulphates, insoluble matter) and is then not at all easily purified; and, secondly, because the carbonate itself is a hygroscopic powder. It seems, then, that there is room for a standard of unquestionable and unalterable purity, and which can be used without any troublesome or risky manipulation.

Iceland spar is sometimes employed, as recommended by Presenius, for verifying the standard of a hydrochloric acid solution, already determined by reference to sodium

carbonate or otherwise. In this case excess of the acid is made to dissolve the whole of a weighed quantity of the spar, and the residual acid is then titrated by a previously standardised alkaline solution. Here, obviously, the Iceland spar is not itself an independent standard. It would become one, however, if so small an excess of acid were employed that no appreciable error could result from the use of a weak alkaline solution of only approximately known strength for the final titration. But this plan may be carried further; for it suggests employment of excess of the Iceland spar, with consequent complete neutralisation of the acid, and the calculation of the standard from the weight of spar dissolved. This method has been tried with encouraging results. The description of the procedure and the details of some test experiments may prove of interest.

Description of the Method.

An approximately normal hydrochloric acid solution is made in the usual way by the use of the hydrometer and tables of specific gravity. Compact fragments of Iceland spar, weighing from about 1 gm. to 3 grms. each, are broken from a larger crystal by pressing with the edge of a knife-blade and smartly tapping the knife with a hammer. These fragments are rinsed with dilute acid to free them from any adhering powder and to round their angles, well washed with distilled water, and dried at above 100° in an air-oven. They are kept for use in a stoppered bottle. One or more of these pieces, weighing altogether from 2½ to 3½ grms., are placed in a clean and dry beaker, and the whole is then accurately weighed. It is not necessary to know the exact separate weight of either beaker or spar. Suitable beakers are of about 20 grms. weight and 80 to 100 c.c. capacity. The beaker is then covered with a watch-glass, and exactly 20 c.c. of the hydrochloric acid are run in from a burette; the point of the burette, the spar in the beaker, and the cover, being so arranged that there can be no loss from the slight spitting that attends the first action. Small flasks may be used in place of beakers, but they are not quite so convenient in the subsequent operations. The covered beaker is then left till the evolution of gas has almost or quite ceased, which is the case in three or four hours. The cover and sides of the beaker are then rinsed down with a little distilled water, the cover replaced, and the beaker raised to the boiling-point and kept at—or about—that temperature for one hour. This drives off dissolved carbonic acid and ensures the completion of the action. Some tendency to bump at the points of contact of the spar and the beaker is overcome by heating it on an asbestos card, with the flame regulated to a suitable size and placed—after boiling has begun—somewhat to one side. As an easy precaution against accident, the beaker may be fixed in position by means of a stout glass rod clamped horizontally and firmly across its cover. Under these conditions the operation hardly requires any watching. After the hour's heating, the perfectly clear and neutral calcium chloride solution is decanted off, and the beaker and its contained residual spar (still in compact lumps) are thoroughly washed with distilled water, dried at about 110°, cooled, and weighed. The difference between the original and final weighings gives the weight of Iceland spar dissolved by, and exactly equivalent to, the 20 c.c. of hydrochloric acid. It also gives, by direct reading and without calculation, the "factor" of the acid or the ratio of its true strength to that indicated by exact normality. For the molecular weight of calcium carbonate is, on the oxygen basis and as exactly as it can be given with present knowledge, 100 (compare the Report of the Committee of the German Chemical Society on Atomic Weights, 1898); and therefore 20 c.c. of a strictly normal acid should dissolve exactly 1 gm. If it is found to dissolve 1.0117 grms., it is 1.0117 times normal; if it dissolves 0.9907 gm., it is 0.9907 times normal; and so on. In practice, two or more such experiments should be conducted simultaneously, and the results may be considered

* Read at the Melbourne Meeting of the Australian Association for the Advancement of Science, January, 1900.

satisfactory if they do not differ by more than about one in a thousand. The residual spar may be returned to the stock bottle for future use.

Possible Sources of Error.

(1). The errors inseparable from a burette measurement need not be discussed. They include the errors of reading, of the burette graduation, and of temperature; but, of these, the second disappears, and the third is reduced to a minimum when readings are compared that are taken from the same part of the same burette and nearly simultaneously. With the burettes now constructed the error of reading is also very small.

(2). Loss of acid by spitting in the early stage and by bumping in the later stage—by which time, however, such loss could hardly be perceptible, as the acid is almost neutralised—is entirely avoided by ordinary precautions, as already described.

(3). Loss of particles of the residual spar during the decantation and washing does not, as a matter of fact, occur. The spar remains in compact pieces, the decanted solution is absolutely clear, and the washing is carried out with the utmost ease.

(4). Solution of a portion of the residual spar in the form of bicarbonate during the action in the cold might be expected to occur to some slight extent. If it did, the expulsion of the carbonic acid by boiling would be accompanied by the re-precipitation of normal carbonate; but not the slightest turbidity is observable.

(5). Incomplete neutralisation of the acid is conceivable, but does not occur if the operation is carried out as described. It has been proved that it does occur, even when boiling is continued for a long time, if but a small excess of spar is employed, *i. e.*, if too small a surface of action is given. A very small residual acidity was found in one case where $1\frac{1}{2}$ grm. was used, the conditions being otherwise as usual; but with the usual amount of $2\frac{1}{2}$ to $3\frac{1}{2}$ grms. the action is always complete.

(6). Solution of some of the spar as normal carbonate, with a corresponding exaggeration of the standard of the acid, seems not unlikely. Fresenius states, on the authority of Hofmann and Weltzien, that the solubility of calcium carbonate in water, after prolonged boiling, is 1 in 28,500 parts, while conductivity methods have given it as about 1 in 77,000. If the small volume of liquid dealt with and the compact nature of the spar be borne in mind, it is evident that any error from this source greater than about 1 in 1000 (or 1 m.grm.) is unlikely; and in practice it is found to be not nearly so great. A very faint alkalinity is just observable in the decanted solution when it is boiled with litmus and compared with an equal quantity of distilled water and litmus, simultaneously boiled. As, however, this alkalinity is more than counterbalanced by a trace of the hydrochloric acid, and as it can be matched by a very few drops of centinormal potash (of which 40 drops would correspond to an error of 1 in 1000), it may safely be neglected.

(7). Action of the acid on the glass beaker need not be feared, as it is not heated till after the acid has been almost totally converted into calcium chloride.

(8). The same remark applies to any conceivable loss of hydrochloric acid by volatilisation.

Advantages of the Method.

(1). Iceland spar is probably as pure a substance as any that the chemist deals with. One of the best values for the atomic weight of calcium is that obtained by Erdmann and Marchand by calcination of the spar. Its purity is, moreover, quite independent of any exertion on the part of the chemist himself. Selected crystals may be bought for a few shillings a pound, and it forms part of the ordinary stock of a chemical laboratory. The other substance employed, hydrochloric acid, is easily obtained in a pure state; but the method does not at all depend on its purity, since only its acidity value is required.

(2). Only one fluid measurement from a burette and two

weighings are involved in each determination, and the rest of the manipulation is of the simplest possible kind. The weighing of the materials (glass and Iceland spar) is not subject to the same errors as that of powders, such as sodium carbonate, or of liquids, such as dilute sulphuric acid. There is no transference of the spar from one vessel to another between the weighings.

(3). As already explained, the result is obtained without arithmetic except for the subtraction of one weighing from another. This is, of course, quite a minor advantage; but it possesses a certain fascination and some practical value.

Test Experiments.

The experiments epitomised in the following table were carried out in the order given and in the manner already described. Those bracketed together were done nearly simultaneously. The four tests of acid C were begun and finished in one day. Some of the others were begun in the evening and allowed to stand overnight before boiling.

In order to test the results by comparison of different experiments not only with the same acid, but with acids of different strengths of known relative value, the second acid was prepared from the first by diluting it in the exact ratio of 100 : 101, and the third acid was prepared in the same way from the second. The calculated and found strengths of these acids are seen to agree.

In order to test the results obtained by this method with those got by reference to other standards, two methods were employed. In the first place a normal solution of sodium carbonate was made in the usual manner. But the bicarbonate used in its preparation, though the best obtainable, was known to be not absolutely pure, as it contained traces of chlorine and insoluble matter; and the brief exposure of the carbonate, while its weight was being finally adjusted on the balance, would tend towards an error in the same direction. The solution might therefore be expected to prove slightly below, though certainly not much below, normal strength. Each sample of acid submitted to the spar test was also titrated with this sodium carbonate solution, using litmus and estimating the end point by direct comparison with distilled water and litmus, the test and the check being boiled simultaneously. The results are given in one column of the table in such a way as to show the strength of the acid on the (probably incorrect) hypothesis that the sodium carbonate was of exactly normal strength, and in another column in such form as to show the true strength of the sodium carbonate on the Iceland spar basis. This is seen to be 0.997 normal, as an average result.

In the second place, estimations were made of the chlorine strength of each sample of hydrochloric acid, except A, by titrating the calcium chloride obtained in the spar test by means of silver nitrate with the chromate indicator. The silver solution, which was approximately decinormal, was exactly standardised by a decinormal salt solution, made with specially purified and fused salt. The calcium chloride solution was made in each case by mixing the whole liquid and washings of a pair of tests and diluting to 500 c.c. This therefore contained the chlorine of 40 c.c. of the hydrochloric acid, and was approximately 0.08 normal. (The test for residual acidity or alkalinity, already referred to, was not applied till after this solution had been made up). The exact strength now found by the silver titration should agree with that given by the Iceland spar test, provided, in the first place, that both standards (sodium chloride and spar) are thoroughly trustworthy, and, in the second place, that the hydrochloric acid was pure in the sense that its acidity was precisely matched by its chlorine contents. No reason was known against either of these assumptions, and they seem justified by the results. These are given in two columns of the table so as to show, first, the strength of the acid on the sodium chloride basis, and, secondly, the strength of the sodium chloride solution on the Iceland spar basis. It is evident that silver solutions may be

Approximately normal HCl.	How made.	Calculated strength of the acid (normal=1).	Grms. of Iceland spar dissolved by 20 c.c. of the acid.	Mean result = strength of the acid by spar standard.	Strength of the acid by titration with "normal" Na_2CO_3 .	Strength of the acid by titration with AgNO_3 (NaCl standard).	Strength of the Na_2CO_3 by the spar standard.	Strength of the NaCl by the spar standard $\times 10$.
A.	Stock	(1'011)	1'0017 1'0107 1'0102 (see Note).	1'0109	1'014	—	0'997	—
B.	A diluted (100:101)	1'001	1'0005 1'0015	1'0010	1'005	1'003	0'996	0'998
C.	B diluted (100:101)	0'991	0'9907 0'9910 0'9913 0'9914	0'9911	0'993	0'991	0'998	1'000
D.	Mixture of acids, ratio not exactly ascertained. ..	—	1'0016 1'0015	1'0015	1'004	1'0015	0'998	1'000

standardised as correctly by indirect reference to Iceland spar as by direct reference to sodium chloride.

All titration values given, except the last one with sodium carbonate, are the means of two or more closely concordant results. The acid was always run from the same part of the same burette, and the other burettes employed were proved to agree with it to within less than 1 in 1000. The flasks employed were not directly compared with the burettes as to capacity; but any small error from this source could affect only the titrations—not the spar tests themselves, into which no flask measurement enters, nor the calculated dilution values to any appreciable extent. During the week in which the experiments were made, and even on single days, the laboratory temperature underwent rather considerable changes, which must account for a large part of the small differences observed, and may possibly explain also certain regularities which they show.

NOTE TO TABLE.—A fourth test of acid A was done simultaneously with the third, but differed from all others in that only about 1½ grms. of the spar were employed. This gave insufficient surface for complete action and caused residual acidity. Its amount was ascertained by titration with centinormal potash, of which 3·8 c.c. were required, corresponding to 0'0019 gm. of CaCO_3 . The result read: Spar dissolved, 1'0085; add for residual acidity, 0'0019; acid standard, = 1'0104. This was the only case of such a correction being required, and for that reason it is excluded from the table.

University of Melbourne.
January 1, 1900.

THE STUDY OF CARBON ELECTRODES.

By J. ZELLER.

THE author, after having pointed out the growing importance of the use of artificial carbon electrodes in the electro chemical industry, touches the question of their resistance to the action of electrolytes and of the products of electrolysis, and, in particular, of chlorine.

The author combats the opinion that the densest carbons would also last the longest. He specially quotes the observations made on the carbons made by Girard and Street, mark E. G., of the Society "Le Carbone," the density of which is 2, and which has a shorter duration than that of electrodes with less density. The same applies to Ceylon graphite.

According to the author the best point of comparison for the valuation of carbons used as electrodes would be the porosity, which is determined in the following manner:—

Let a be the true density of the carbon, taken on the powder, and b the apparent density. The porosity in terms of the true density is expressed as follows—

$$p = 100 \frac{(a-b)}{a}.$$

If we admit with Winteler that the disaggregation of the carbons is principally due to the mechanical action of the gases, we should conclude that the less porous carbons are also the best.

Finally, we must take into account the relationship between the specific resistances of the carbon and of the liquid submitted to electrolysis. If the carbon has a higher resistance than the electrolyte, the density of the current in the electrodes would be greater in their upper portions, and consequently the disaggregation would be greater in this part, the result being that the carbons would have a tendency to break off at the level of the electrolyte. In the contrary case the carbons taper off, and become gradually thinner from the level of the liquid to the bottom. It is therefore necessary to make certain of having a uniform density of current at the surface of the electrodes, by proportioning as far as possible the two specific resistances of the electrodes and of the electrolyte. —*Zeits. fur. Elektr.*, 1899, vi., No. 40.

THE ESTIMATION OF IODIC ACID IN NITRATE OF SODA.

By R. AUZENAT.

It is of importance to be able to exactly estimate the iodic acid present in raw nitrate of soda, certain samples containing as much as 1 or 2 per cent of iodate of soda.

The Beckurts method is rather qualitative, that of Rammelsberg is only applicable to the estimation of iodates in the presence of acids which have no action on iodide of potassium; however, by slightly modifying this latter method I succeeded in effecting the estimation in nitrates.

If to a solution of an iodate containing iodide of potassium, we add a small quantity of sulphuric acid, the iodic acid reacts on the iodide of potassium, setting iodine at liberty; agitation with a solvent, such as bisulphide of carbon or benzene, causes the iodine to pass into this medium, giving it a violet colour. In the presence of a nitrate, even when dilute, sulphuric acid sets free nitric acid, which decomposes the iodide of potassium; the perchlorate of potash which exists in the raw nitrates, acts in the same manner. If, on the contrary, we add a very small quantity of acetic acid to a dilute solution of the nitrate, the iodic acid reacts only on the iodide, and gives the liquid a caramel-yellow colour.

For its estimation I proceed in the following manner:—

In a test-tube rack, having the base covered with white paper, I placed six test-tubes of the same size, 25 m.m. diameter and 18 c.m. high; a mark on each shows the level of 50 c.c. In the first I place 10 c.c. of a solution of iodate of potassium containing 1 grm. per litre; in the second, 30 c.c. of a solution of the raw nitrate containing 33 grms. per litre; in the third, 35; in the fourth, 40; in the fifth, 45; and in the sixth, 50 c.c. To each of the first five tubes I add distilled water up to the mark, then to all six 2 c.c. of a solution of iodide of potassium at 10 per cent, and, as rapidly as possible, five drops of glacial acetic acid.

The caramel colour immediately appears and becomes homogeneous after a slight agitation. At the end of ten minutes we note which tube corresponds with the colour of the standard tube. If the five tubes are all darker coloured than the standard tube, we repeat the experiment with 20 c.c., or even more, of the titrated solution of iodate; if the five tubes are less deeply coloured than the other one, we, on the contrary, reduce the amount of iodate.

It is indispensable to fill all the tubes afresh for each experiment, as the colour changes with the time, and the comparison could not otherwise be made under the same conditions as to time.

Thus, with tubes of a lighter colour than the standard, the titration would be impossible by the addition of the typical solution to one of them, until the colours were identical.

Under the conditions shown above, the estimation can be made with the same rapidity, and the same exactitude as the estimation of ammonia with Nessler's solution.—*Moniteur Scientifique*, Series 4, xiv, February, 1900.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART II.

TUNGSTEN AND MOLYBDENUM.

By HARRY BREARLEY.

(Concluded from p. 65).

MOLYBDENUM.

I. SEPARATION FROM OTHER ELEMENTS.

275. *Iron*.—GENTELE (C. N., iii, 223).—Molybdates of iron are formed when neutral $(\text{NH}_4)_2\text{MoO}_4$ is added to a ferric solution. (Such combinations prevent the perfect separation of Mo from Fe, Cr, and Al by ammonia, &c.—H. B.).
- 275a. BAMBER (J. I. S. I., 1894, i, 319).—Dissolve steel in HNO_3 , add Na_2CO_3 , but not to alkalinity, evaporate, ignite to dull redness, and digest with dilute Na_2CO_3 . Mo, P, S, Cr, and Va are dissolved out. Mo and Va generally occur in basic pig containing Cr.
276. *Phosphorus*.—DEBRAY (C. N., xvii, 183).—The phospho-molybdic acid, mixed with lime, is heated in successive currents of H_2S and HCl. Wash with water and with HCl, and filter off molybdenum sulphide.
277. REICHHARDT (C. N., xxviii, 315).—Dissolve in sodium carbonate, and precipitate P with magnesia mixture.
278. *Chromium*.—BENNEVILLE (J. I. S. I., 1895, i, 206).—Chromium precipitated with excess of ammonia; operation needs repeating (see 281a).
279. *Tin*.—CLARKE (C. N., xxi, 124).—Metals precipitated as sulphides, and the stannic compound redissolved by a faint HCl solution of oxalic acid. W behaves erratically.
280. *Arsenic*.—FRIEDHEIM and MICHAELIS (J. C. S., lxxviii, 415).—Arsenic is distilled after mixing with methyl alcohol and HCl. The separation from

tungsten is less perfect; they may, however, be precipitated together with HgNO_3 , and the As estimated by difference.

281. *Vanadium*.—CARNOT (J. C. S., lii, 897).—Va is precipitated from ammoniacal solution containing $(\text{NH}_4)\text{Cl}$ as manganese vanadate. Like separation of W not complete. (See also 298).
- 281a. *Various*.—BREARLEY (C. N., lxxix, 2).—Ba is precipitated with H_2SO_4 from HCl solution. By precipitating as PbMoO_4 in modified ways Ba, Ca, Sr, As, Cd, P, Al, Ur, and those elements named already (283) do not interfere. Silicates give slightly high results. Fe and Cr are separated at boiling-point with soda hydrate. Separation of Cr with ammonia (278) not good.

II. GRAVIMETRIC ESTIMATIONS.

282. CHATARD (C. N., xxiv, 175).—Mo precipitated with lead acetate, ignited apart from filter, and weighed as PbMoO_4 . Analogous process for tungsten frustrated by fineness of the precipitate. (See 243).
283. BREARLEY (C. N., lxxviii, 203).—Critical examination of Chatard's process. PbMoO_4 may be ignited with the paper. Prolonged heating at high temperature causes only slight loss. Presence of excess acetic acid, lead acetate, alkaline nitrates, chlorides, or acetates, and salts of the metals Mn, Cu, Co, Ni, Zn, Mg, Hg are without influence. Schindler's volumetric process (295) supplemented by a more delicate end-reaction.
284. VON DER PFORDTEN (C. N., i, 18).—Precipitation with HgNO_3 and reduction in hydrogen.
285. JANNASCH and WASOWICZ (C. N., lxxvi, 6).—Similar to 284.
286. MOISSAN (C. N., lxxii, 2).—Precipitates as mercurous molybdate, and determines as bioxide. (This admirable paper gives an account of the preparation and numerous properties of metallic Mo.—H. B.).
287. SMITH and BRADBURY (J. C. S., lxii, 241).—Same available precipitants as for W (see 261). Suggest the estimation of W and Mo together as Cd salts and electro-estimation of Cd in another portion as a means of determining W and Mo in mixtures.
288. PECHARD (C. N., lxx, 89).—Volatilised in HCl gas as $\text{MoO}_3 \cdot 2\text{HCl}$. The compound is dissolved in water, evaporated, and MoO_3 weighed. Tungstates are not at all volatilised, and may be thus separated (234 and 235).
289. SMITH and HOSKINSON (C. N., liii, 278).—Deposited electrolytically from acid solution of the molybdates as $\text{Mo}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and so weighed, or ignited to MoO_3 .
- 289a. HEIDENREICH (J. S. C. I., 1896, 744).— Mo_2O_3 is not completely deposited from solution of $(\text{NH}_4)_2\text{MoO}_4$ in four days.
290. FRIEDHEIM and EULER (J. C. S., lxxviii, 535).—Precipitated as sulphide, filter, ignited short of losing Mo, digested with $(\text{NH}_4)\text{HO}$, evaporated, and ignited to MoO_3 .
291. TAGGART and SMITH (J. C. S., lxxii, 433).—Mo sulphide ignited with oxalic acid burns to pure MoO_3 .

III. VOLUMETRIC ESTIMATIONS.

292. WERNCKE (C. N., xxxii, 259).—In Pisani's process (reduction with Zn and titration with permanganate) the reduction is not to the sesquioxide. Sodium amalgam does not effect a complete reduction. The results are mutually comparable.
293. BENNEVILLE (J. I. S. I., 1895, i, 228).—Pisani's process. The temperature at which the reduction is made has no influence on results; nitric acid must be absent; H boiled off before titrating.
294. VON DER PFORDTEN (C. N., i, 18).—HCl solution reduced and titrated in presence of H_2SO_4 and MnSO_4 . Similar process for W; the reduced solu-

- tion (red) added to excess permanganate; excess estimated with FeSO_4 .
295. SCHINDLER (C. N., lviii., 61).—Faintly acetic solution precipitated with standard lead acetate, using tannin as indicator. Lead may be estimated inversely (see 283).
296. SEUBERT and POLLARD (C. N., lxxii., 293).— MoO_3 is dissolved in standard soda and excess titrated with HCl and phenolphthalein.
297. FRIEDHEIM (C. N., lxxv., 91).—Molybdate decomposed with KI and HCl ; iodine absorbed and titrated with thiosulphate. A discussion of modified process by Gooch and Fairbanks. Gooch defends his modifications (C. N., lxxv., 208; and C. N., lxxviii., 207).
298. FRIEDHEIM and EULER (Z. C. S., lxxviii., 535).—By distilling first with HCl and HBr , and then with HCl , KI , and phosphoric acid, both Va and Mo are estimated from the Br and I liberated.

IV. DETECTION AND MISCELLANEOUS NOTES.

299. SCHLOSBERGER (C. N., iii., 192 and 204).—Dilute solution of $(\text{NH}_4)_2\text{MoO}_4$ gives blue colour with a soluble sulphide.
300. SKEY (C. N., xvi., 324).—An HCl solution shaken with zinc gives a red colour, which detects one part in two millions. Fe does not interfere if time be allowed it to deoxidise. W gives a like colour. (See also ELBRAM, Z. C. S., lxxii., 522).
301. MOISSAN (C. N., lxxii., 2).—Heated with phosphorus perchloride, reddish fumes condense in a ring.
302. SCHONN (C. N., xxi., 166).—Heated with H_2SO_4 a blue colour appears. MASCHKE (C. N., xxxviii., 22) describes a more convenient and certain modification of the test.
303. SMITH (Z. C. S., lxiv., 171).—Mo precipitates Ag from ammoniacal AgCl quantitatively; similarly from solutions of auric chloride; tungsten acts in a similar way; Mo and W (less readily) reduce HgCl_2 . (Would these reactions serve to measure the oxidation of metallic W and Mo powders?—H. B.). MoO_2 also precipitates Ag. (See SMITH and SHINN, C. N., lxx., 197; also No. 264).
304. MONTEMARTINI (Z. C. S., lxii., 1402).—Strong HNO_3 attacks Mo slowly; more dilute acids do not at once convert what they dissolve into MoO_3 .
305. GUICHARD (Z. C. S., lxxii., 496).—Mo alone is formed on igniting MoO_3 in hydrogen at 600°C .
306. ISELSTRÖM (Z. C. S., lxxviii., ii., 505).—In Swedish hæmatite Mo_2O_3 was found up to 9 per cent.

ON GADOLINIUM.*

By C. BENEDICKS.

(Concluded from p. 63).

Gadolinium Nitrate.—I. $\text{Gd}(\text{NO}_3)_3 \cdot 6\frac{1}{2}\text{H}_2\text{O}$, is obtained as large soluble asymmetrical crystals, over sulphuric acid, or by free evaporation in air.

Analysis.

	I.	II.	
Gd ..	33'97	33'80 per cent.	Calculated 33'99 p. c.
3NO_3 ..	—	—	" 40'52 "
$6\frac{1}{2}\text{H}_2\text{O}$..	—	—	" 25'49 "
Mean specific gravity ..	..	..	2'332
Molecular volume ..	..	..	196'8

2. $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, crystallises from concentrated nitric acid in beautiful monosymmetric prisms, which gradually become moist in air, and therefore are not suited to measurement.

	Analysis.			
	I.	II.	III.	Calculated
Gd ..	35'85	35'95 p. c.	—	36'11 p. c.
3NO_3 ..	—	—	42'81 p. c.	" 43'06 "
$5\text{H}_2\text{O}$..	—	—	—	" 20'83 "
Mean specific gravity ..	..	..	..	2'406
Molecular volume ..	..	..	..	179'5

Gadolinium Ammonium Nitrate was obtained as long, hair-fine, deliquescent needles, from a solution almost solidified over H_2SO_4 , containing the respective nitrates in the proportion $1\text{Gd}_2(\text{NO}_3)_3 : 2\text{NH}_4\text{NO}_3$. This falls in with the idea that gadolinium remains in the first mother-liquors with the yttrium metals, on the ammonium double nitrate crystallisations, whilst lanthanum, cerium, praseodymium, &c., crystallise out.

Gadolinium Sulphate, $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, was obtained as small sparkling crystals at the ordinary temperature or on the water-bath. Crystalline form monoclinic, isomorphous with yttrium sulphate, $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.

	Analysis.			
	I.	II.	III.	Calculated
Gd_2O_3 ..	—	—	—	48'39 p. c.
3SO_3 ..	—	—	—	" 32'26 "
$8\text{H}_2\text{O}$..	19'51	19'46	19'64 p. c.	" 19'35 "
Specific gravity ..	..	..	..	3'010
Molecular volume ..	..	..	..	247'2

Anhydrous Gadolinium Sulphate, $\text{Gd}_2\text{O}_3(\text{SO}_4)$.

Specific gravity ..	..	..	..	4'139
Molecular volume ..	..	..	..	145'0

Solubility determinations of the sulphate were conducted by dissolving small portions of the anhydrous salt by stirring in water, and then shaking the solution four to five hours, automatically, in a water-bath at the required temperatures. The graphic representation of the results shows that the solubility is much greater at 93° to 106° than at higher temperatures, the numbers obtained probably bearing a relation to the presence of a sulphate containing varying amounts of water.

Gadolinium Potassium Sulphate,—

$\text{Gd}_2\text{O}_3(\text{SO}_4) + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$, was obtained as large crystals on the water-bath from a solution containing $\text{Gd}_2\text{O}_3(\text{SO}_4) + 3\text{K}_2\text{SO}_4$.

	Analysis.		
	I.	II.	Calculated
Gd_2O_3 ..	44'49 per cent.	—	44'43 per cent.
3SO_3 ..	—	—	29'62 "
K_2SO_4 ..	21'77 "	—	21'51 "
$2\text{H}_2\text{O}$..	4'39 "	—	4'44 "
Specific gravity ..	..	..	3'503
Molecular volume ..	..	..	231'4

Solubility in Saturated K_2SO_4 Solution.—According to my determinations, 100 c.c. saturated K_2SO_4 solution contains 0'87—0'77 gm. Gd_2O_3 ; according to Bettendorff, as the mean of three experiments, 0'77 gm. Gd_2O_3 .

Gadolinium Selenate, $\text{Gd}_2(\text{SeO}_4)_3 \cdot 10\text{H}_2\text{O}$, crystallises over sulphuric acid at the ordinary temperature in large clear prisms. The salt is isomorphous with the selenates of yttrium and erbium, whose formula given by Cleve is $\text{R}_2(\text{SeO}_4)_3 \cdot 9\text{H}_2\text{O}$. A water content of $10\text{H}_2\text{O}$ agrees better, however, with his analysis results.

This salt decomposes rapidly, especially in the warm, wherefore crystallographic measurement is rather difficult. The crystalline form is rhombic.

	Analysis of Salt.			
	I.	II.	III.	Calculated
Gd_2O_3 ..	38'95	38'82	—	39'57 p. c.
3SeO_3 ..	—	—	—	41'39 "
$10\text{H}_2\text{O}$ [20'67]	[20'48]	20'11	—	19'54 "
Specific gravity ..	..	..	..	3'048
Molecular volume ..	..	..	..	302'3

* Zeitschrift für Anorganische Chemie, xxii., 5, p. 393.

2. $\text{Gd}_2\cdot 3(\text{SeO}_4) + 8\text{H}_2\text{O}$ was obtained on the water-bath as large beautiful crystals, with somewhat the sheen of mother-of-pearl.

The salt is isomorphous with yttrium sulphate, $\text{Y}_2\cdot 3(\text{SO}_4) + 8\text{H}_2\text{O}$.

Analysis.

	I.	II.	Calculated
Gd_2O_3	—	—	40·66 per cent.
3SeO_3	—	—	43·07 "
$8\text{H}_2\text{O}$	16·18	16·25 p. c.	16·27 "
Specific gravity	..	..	3·309
Molecular volume [.. .. .	..	..	267·5

Anhydrous Gadolinium Selenate, $\text{Gd}_2\cdot 3(\text{SeO}_4)$, is obtained by heating the above selenate to 130° .

Analysis.

	I.	II.	Calculated
Gd_2O_3	47·76	47·80	48·56 p. c.
3SeO_3	[50·15]	51·61 "	51·44 "
Specific gravity	..	..	4·175
Molecular volume	..	..	177·5

Gadolinium Potassium Selenate,—

$\text{Gd}_2\cdot 3(\text{SeO}_4) + 3\text{K}_2\text{SeO}_4 + 4\text{H}_2\text{O}$, was obtained on the water-bath as microscopically small needles.

Analysis.

	I.	II.	Calculated
Gd_2O_3 ..	24·99 per cent.	—	24·36 per cent.
6SeO_3 ..	50·95 "	—	51·61 "
$3\text{K}_2\text{O}$..	—	—	19·15 "
$4\text{H}_2\text{O}$..	4·71 "	—	4·88 "

Acid Gadolinium Selenite, $\text{Gd}_2\cdot 3(\text{SeO}_3) + \text{H}_2\text{SeO}_3 + 6\text{H}_2\text{O}$, was obtained by precipitating a solution of $\text{Gd}_2\cdot 3(\text{CH}_3\text{CO}_2)$ with $\text{Na}_2\text{SeO}_3 + \text{H}_2\text{SeO}_3$, when an amorphous precipitate was formed which gradually passed into small needles.

Analysis.

	I.	II.	Calculated
Gd_2O_3 ..	—	38·94 per cent.	38·69 p. c.
4SeO_2 ..	48·05	—	47·77 "
$2\text{H}_2\text{O}$..	—	—	3·87 "
$5\text{H}_2\text{O}$..	9·46	—	9·67 "

Gadolinium Hyposulphate.—From a solution obtained from gadolinium sulphate and barium hyposulphate, little crystals deposited themselves which proved to be gadolinium hyposulphate. The solution solidified, after prolonged concentration over H_2SO_4 , to a crystalline mass, very deliquescent, and incapable of analysis.

Gadolinium-ethyl Sulphate, $\text{Gd}_2\cdot 3(\text{C}_2\text{H}_5\text{SO}_4) + 9\text{H}_2\text{O}$, obtained by double decomposition of gadolinium sulphate and barium-ethyl sulphate. The crystals are transparent rounded plates.

Analysis.

	I.	II.	Calculated
Gd	22·57	22·59 p. c.	22·51 p. c.
$3\text{C}_2\text{H}_5\text{SO}_4$..	—	—	54·11 "
$9\text{H}_2\text{O}$	—	—	23·38 "
Specific gravity	..	..	1·923
Molecular volume	..	..	360·4

Gadolinium Vanadate. $\text{Gd}_2\cdot 3\cdot 5(\text{V}_2\text{O}_5) + 26\text{H}_2\text{O}$, obtained by precipitating a neutral gadolinium nitrate solution with a concentrated solution of sodium bivanadate and filtering off the precipitate. Crystals soon form in the filtrate.

Analysis.

	I.	II.	Calculated
Gd_2O_3 ..	21·02 per cent.	—	20·69 per cent.
$5\text{V}_2\text{O}_5$..	52·04 "	—	52·41 "
$26\text{H}_2\text{O}$..	26·93 "	—	26·90 "
Specific gravity	..	..	2·660
Molecular volume	..	..	654·1

Gadolinium Carbonate.

1. Basic Carbonate, $\text{Gd} \left\{ \begin{array}{l} \text{OH} \\ \text{CO}_3 \end{array} \right. + \text{H}_2\text{O}$ (dried at 100°).

A crystalline carbonate is obtained by passing CO_2 into cold water in which gadolinium hydroxide is suspended.

Analysis.

	I.	II.	Calculated
Gd_2O_3 ..	72·21	72·22 p. c.	72·58 p. c.
2CO_2 ..	17·85	17·07 "	17·74 "
$3\text{H}_2\text{O}$..	—	—	9·68 "

2. Neutral Carbonate, $\text{Gd}_2\cdot 3(\text{CO}_3) + 13\text{H}_2\text{O} (?)$. If CO_2 is passed in for a still longer time, it is observable through the microscope that the fine needles of the basic carbonate pass into larger oval crystals. It was not possible to get a constant weight, even after drying these crystals at 100° for three days.

Analysis.

	I.	II.	Calculated
Gd_2O_3 ..	49·35	49·66 p. c.	49·59 p. c.
3CO_2 ..	—	[15·74] "	18·18 "
$13\text{H}_2\text{O}$..	—	—	32·23 "

Gadolinium Oxalate, $\text{Gd}_2\cdot 3(\text{C}_2\text{O}_4) + 10\text{H}_2\text{O}$, a fine crystalline precipitate, which can be obtained from concentrated HNO_3 as large monoclinic crystals. On heating to 110° the salt loses $6\text{H}_2\text{O}$.

Analysis of Salt, dried in Air.

	I.	II.	Calculated
Gd_2O_3 ..	47·33 per cent.	—	47·62 per cent.
$3\text{C}_2\text{O}_3$..	—	—	28·57 "
$10\text{H}_2\text{O}$..	—	—	23·81 "

According to Brauner, gadolinium should stand between neodymium and praseodymium, judging by his results for the solubilities of the three corresponding oxalates in 100 c.c. normal sulphuric acid, and which are respectively 0·10034 grm., 0·1095 grm., and 0·12327 grm.; therefore, gadolinium oxalate belongs to the oxalates of the rare earths most insoluble in acids.

Gadolinium Acetate, $\text{Gd}_2\cdot 3(\text{C}_2\text{H}_3\text{O}_2) + 4\text{H}_2\text{O}$, obtained from the solution of the oxide in acetic acid, as difficultly soluble, clear, asymmetric crystals, isomorphous with the corresponding yttrium compound.

Analysis.

	I.	II.	Calculated
Gd_2O_3 ..	44·5	44·64 p. c.	44·44 p. c.
$3\text{C}_2\text{H}_3\text{O}_3$..	—	—	37·78 "
$8\text{H}_2\text{O}$..	18·09	—	17·78 "

Specific gravity 1·611
Molecular volume 251·4

Gadolinium Propionate $\text{Gd}_2\cdot 3(\text{C}_3\text{H}_5\text{O}_2) + 3\text{H}_2\text{O}$, obtained as large rhombic crystals in the vacuum desiccator.

Analysis.

	I.	II.	Calculated
Gd_2O_3 ..	41·96	42·04 p. c.	41·96 p. c.
$3\text{C}_3\text{H}_{10}\text{O}_3$..	—	—	45·45 "
$6\text{H}_2\text{O}$..	12·65	12·41 "	12·59 "

Conclusions.

From these experiments it is evident that gadolinium is closely allied to the yttrium metals, and resembles the cerium metals to a much slighter degree. Therefore a small intermediate group is formed of samarium and gadolinium,

For trivalent elements, most characteristic are the platinumchloride and gold chloride double salts, the potassium double sulphate, the selenite, the ethyl sulphate, and the basic carbonate of gadolinium.

Nothing can yet be definitely stated with regard to the position of gadolinium in the periodic system, but it will certainly find place in the eighth horizontal row.

PREPARATION OF GRAPHITOIDAL SILICON.*

By FREDERICK S. HYDE.

THE analogy between silicon and carbon in their allotropic modifications, especially the graphitic, and the existence of a crystalline compound of silicon and carbon, known as carborundum, have tended to create doubt as to the purity of graphitoidal silicon, yet the production of the latter seems to be based on reactions favouring the exclusion of carbon.

The usual methods involve the reduction of potassium-silico-fluoride with aluminum or metallic sodium; or the reduction of pulverised white sand with magnesium powder.

The method submitted depends on the reduction of finely pulverised white sand with magnesium powder and the subsequent fusion of the reduction-product with cryolite and aluminum, to form an alloy of aluminum and silicon, from which the latter is obtained on treatment with hydrochloric acid.

For experiment take :—

	Grms.
Finely pulverised white sand.. .. .	12
Magnesium powder.. .. .	3

Mix thoroughly, place in a dry test-tube, supported by a clamp on a ring stand, warm gently, and then commencing at the lower end ignite cautiously with the burner in hand.

There may be a slight separation of the contents due to the expansion of air or moisture, which should be remedied. As the heat becomes concentrated at the lower end, the contents become darker, resulting in a quiet incandescence which creeps toward the upper part, usually completing the reaction with a slight puff. The exterior surface of the test-tube assumes a greenish black lustrous appearance, and becomes wrinkled or "buckled" from the heat of the reaction. Remove the contents, which are brownish-black in colour; pulverise and mix with a sufficient quantity of cryolite powder.

Introduce the mixture into a small Denver crucible, containing a piece of aluminum (walnut size) on the bottom. The cryolite serves as a vehicle for incorporating the reduction product with the aluminum and as a flux for impurities. Place the crucible in a small gas furnace and apply blast.

As soon as the aluminum liquefies, stir the mass thoroughly with an iron rod. Quite a little stirring is necessary in order that the molten aluminum may be brought into contact with every portion of the reduced mass. Near the final stage, fumes and tongues of bluish flame, like burning zinc, may be observed on the surface. Allow to cool.

Remove the regulus, which should have a brilliant silver-white crystalline surface, and examine the blackened slag for any small globules of alloy. Place the regulus and globules in a porcelain dish or casserole, and treat with warm hydrochloric acid. As the aluminum dissolves, black glistening spangles of silicon separate out of the solution. Decant and wash with clear water. Then wash with alcohol and dry on the filter.

Some employ zinc to form the alloy, but aluminum is preferable for the following reasons not stated in the textbooks :—

First.—Zinc melts and volatilises at a comparatively low temperature, before the silicon has a chance to become properly alloyed. It is also difficult to combine the reaction-product with molten zinc, since the latter is heavier and causes the former to float.

Second.—The copious white fumes and blue flame evolved by zinc, even though the crucible be covered and the oxidation minimised, cause large amounts of "zinc

wool" to condense on the interior of furnace and crucible, thus interfering with the operation.

Third.—The zinc-silicon alloy is hard and resists solution with hot or cold hydrochloric acid, while the aluminum alloy is readily dissolved.

Fourth.—Zinc tends to produce needle-shaped crystals of silicon, which are not so striking as the graphitoidal spangles obtained from the aluminum alloy.

Graphitoidal silicon resists oxidation before the blow-pipe. Under the microscope, by reflected light, the faces of incomplete octahedra are visible in the small irregularly shaped masses. The yield is rarely more than 10 per cent by weight of the silica employed.

There are indications that the element silicon itself, heretofore classed among laboratory curiosities, may become commercially important.

On account of its high electrical resistance, its use in the form of compact rods has already been suggested for electric heating apparatus.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 1st, 1899.

Professor THORPE, F.R.S., President, in the Chair.

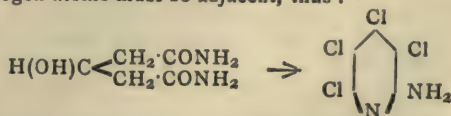
CERTIFICATES were read for the first time in favour of Messrs. Frank Curzon Britten, 21, Osbaldeston Road, London, N.; Robert Eadie, junr., 31, Clarendon Street, Partick, N.B.; Morris Broad Fowler, 30, West Park, Clifton, Bristol; Reginald Gordon Halstead, 3, Rathbone Place, Oxford Street, London, W.; James Henry Kershaw, 21, Richmond Park Road, Kingston-on-Thames; Thomas Macara, 6, West Bank Terrace, Hillhead, Glasgow; James Walter Tilley, 2, Stockwell Crescent, London, S.W.; Augustus John Walker, 3, Arnold Street, Hull.

Of the following papers, those marked * were read :—

*8. "The Chlorine Derivatives of Pyridine. Part V. Constitution of Citrazinic Acid. Formation of $\alpha\alpha'$ -Dichloropyridine and of $\alpha\alpha'$ -Diiodoisonicotinic Acid." By W. J. SELL, M.A., and F. W. DORTON, M.A.

Although its genetic relationships leave little room for doubt that in citrazinic acid the hydroxyl groups occupy the $\alpha\alpha'$ -positions relatively to the nitrogen, in view of the importance of this compound and its derivatives it was deemed expedient to obtain confirmatory evidence. This was done as follows :—

The diamide of β -oxyglutaric acid was prepared and treated with phosphorus pentachloride, when aminotetrachloropyridine was obtained. In this compound, the nitrogen atoms must be adjacent, thus :—

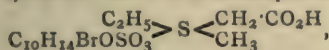


By the action of phosphorus pentachloride on citrazinic acid, dichloroisonicotinic acid was obtained by Behrmann and Hofmann (*Ber.*, 1884, xvii., 2694), and by the authors (*Trans.*, 1897, lxxi., 1069), and this interacts with ammonia to form aminochloroisonicotinic acid. (*Trans.*, 1897, lxxi., 1075), which substance, on further treatment with phosphorus pentachloride, loses its carboxyl group, and yields an aminotetrachloropyridine identical with that mentioned above. These changes may be represented thus :—

* Contributions from the Havemeyer Laboratories of Columbia University. From the *American Chemical Journal*, vol. xxi., No. 8.

less microscopic prisms melting at 115–117°. When pure, it is not hygroscopic, but is extremely soluble in water, alcohol, or acetone.

Methylethylthetine dextro-α-bromocamphorsulphonate,—



was prepared in a similar manner; it is sparingly soluble in cold acetone, and crystallises in silky white needles melting at 166–168°.

The molecular rotatory powers of these salts in dilute aqueous solution are the molecular rotatory powers of the optically active acid ions, so that the basic thetine group possesses no optical activity; no resolution of the asymmetric thetine into optically active components occurs, because more than one-half of the thetine bromide can be isolated as the pure optically active sulphonate. It is further most improbable that both salts are partially racemic and contain a dextro- and a laevo-thetine radicle, because partially racemic substances are of very rare occurrence.

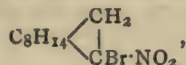
The conclusion is drawn that, if sulphur really exists as a quadrivalent element in these salts, the four atoms directly and independently attached to the sulphur atom lie in the same plane as the latter, and that quadrivalent sulphur cannot lead to enantiomorphous configurations.

Previous attempts to prepare salts of asymmetric thetines and sulphonium compounds with optically active acids have invariably led to uncrystallisable products; the present are therefore the first observations from which information can be derived respecting the space configuration of quadrivalent sulphur compounds.

The investigation of these and allied substances is being continued.

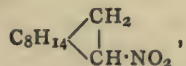
*II. "Nitrocamphane." By M. O. FORSTER.

The compound, $\text{C}_{10}\text{H}_{16}\text{O}_2\text{NBr}$, obtained by the action of potassium hypobromite on camphoroxime (*Trans.*, 1899, lxxv., 1141), is a *bromonitrocamphane*,—



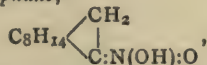
although it gives Liebermann's reaction for nitroso-derivatives.

Nitrocamphane,—



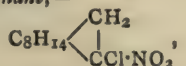
prepared by reducing bromonitrocamphane with alcoholic potash, melts at 147–148°, and has the specific rotatory power $[\alpha]_D +4.5^\circ$ in alcohol; it gives Liebermann's reaction for nitroso-derivatives, and is indifferent towards alcoholic ferric chloride.

Pseudonitrocamphane,—



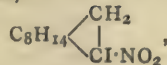
obtained on acidifying a solution of nitrocamphane in caustic potash, melts at 74°, and has $[\alpha]_D -95^\circ$ (approximately); it develops a deep cherry-red colouration with ferric chloride, and changes spontaneously into the normal modification either in the solid or dissolved state. In the latter condition, this transformation is accelerated by the influence of piperidine, alkalis, and sunlight. It forms a *potassium* derivative, a *benzoyl* derivative, and a *pseudonitrole*.

Chloronitrocamphane,—



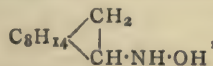
produced when sodium hypochlorite acts on camphoroxime, or when chlorine water is added to a solution of nitrocamphane in caustic alkali, melts at 217°, and has $[\alpha]_D -53.1^\circ$ in alcohol; it gives Liebermann's reaction for nitroso-derivatives.

Iodonitrocamphane,—



precipitated from solutions of nitrocamphane in potash by iodine dissolved in potassium iodide, melts at 179°, and has $[\alpha]_D -10.8^\circ$ in alcohol; it gives Liebermann's reaction.

Hydroxylaminocamphane (bornylhydroxylamine),—



prepared by reducing nitrocamphane with aluminium amalgam, crystallises from petroleum in small, oblong plates and melts at 154°; it dissolves in hot water, and the cold solution reduces ferric chloride, ammoniacal silver nitrate, and Fehling's solution, almost immediately.

12. "The Absorption Spectra of Ammonia, &c." By W. N. HARTLEY, F.R.S., and JAMES J. DOBBIE, D.Sc., M.A.

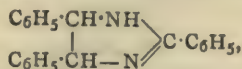
It was shown by Soret, and subsequently by Hartley and Huntington, that the purest forms of commercial ammonia which could be purchased (even that stated to be "volcanic ammonia"), contained some substance which exhibited an absorption band which was believed to be due to traces of some constituent of gas-liquor. There was distinct evidence that the band was due to an impurity (*Phil. Trans.*, Part I., 1879, p. 267). An aqueous solution of ordinary ammonia, 150 m.m. in thickness, containing 2.5 grms. ammonia in 100 c.c., gives a broad absorption band between $1/\lambda$ 3694 (λ 2707) and $1/\lambda$ 4306 (λ 2322). This band becomes less marked when the ammonia is converted into ammonium chloride, and this recrystallised repeatedly. It is altogether absent from ammonia prepared from ammonium oxalate which has been carefully purified by crystallisation. It is also absent from ammonia prepared by the reduction of hydroxylamine hydrochloride. The authors conclude therefore that the absorption shown by ordinary aqueous ammonia is due to an impurity which is not of inorganic origin, but is more probably due to pyridine bases. They have, in fact, found that ordinary strong ammonia is contaminated with pyridine bases to the extent of about 0.00014 per cent.

They have measured also the continuous absorption of a normal solution of ammonia 200 m.m. and 100 m.m. in thickness. Methylamine hydrochloride and hydroxylamine hydrochloride show no selective absorption and are both highly diacinic. A solution of the former, 150 m.m. in thickness, containing 2.5 grms. methylamine in 100 c.c. distilled water, shows practically no absorption, whilst a layer of the latter of the same thickness and strength transmits the whole spectrum with the exception of a few lines at the extreme violet end.

Acetaldoxime and acetoxime show considerable general absorption, but no selective absorption. A solution of acetaldoxime 150 m.m. in thickness, containing 1.25 grms. acetaldoxime in 100 c.c. of water, absorbs all lines beyond $1/\lambda$ 3323 (λ 3009); a layer 25 m.m. in thickness of a solution containing 1 milligram-molecule dissolved in 20 c.c. of water gives a continuous spectrum to $1/\lambda$ 3952 (λ 2530). Acetoxime shows slightly greater absorption than acetaldoxime, due to the additional methyl group.

13. "Isoamarine." By FRANCIS R. JAPP, F.R.S., and JAMES MOIR, M.A., B.Sc.

In a recently published note (*Proc.*, 1899, xv., 211), the authors showed that both ordinary amarine and the isoamarine of Snape and Brooke (m. p. 198°) have the structure—



differing only in their configuration; the former being the meso-, the latter the racemic, form. The correctness of this view of the constitution of isoamarine was confirmed

by heating *r*-diphenylethylenediamine with benzoic acid, and subsequently by its re-resolution into the enantiomorphs by Snape (*Proc.*, 1899, xv., 228).

Feist and Arnstein, however, by heating *s*-dibenzoyl-*r*-diphenylethylenediamine in a current of gaseous hydrogen chloride, claim to have prepared an isoamarine melting at 175°, structurally identical with the foregoing (*Ber.*, 1895, xxviii., 3177). As a third configuration—apart from those of the separate enantiomorphs, of which there can be no question here—is contrary to what theory predicts, we resolved to re-examine this compound.

We find that it melts at 198° instead of at 175°, and is in every respect identical with the isoamarine of Snape and Brooke.

The compound is so easy to purify that the wrong melting-point given by Feist and Arnstein is doubtless a mere inadvertence.

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 9th, 1900.

Prof. LODGE, F.R.S., President, in the Chair.

THE following Officers were elected to form the Council:—

President—Professor Lodge.

Vice-Presidents, who have filled the Office of President—

Dr. Gladstone, Prof. Carey Foster, Prof. Adams, Lord Kelvin, Prof. Clifton, Prof. Reinold, Prof. Ayrton, Prof. Fitzgerald, Prof. Rucker, Sir W. Abney, Mr. Shelford Bidwell.

Vice-Presidents—Mr. Blakesley, Mr. Boys, Prof. Everett, Mr. Griffith.

Secretaries—Messrs. H. M. Elder and W. Watson.

Foreign Secretary—Prof. S. P. Thompson.

Librarian—Mr. W. Watson.

Treasurer—Prof. Callendar.

Other Members of Council—Prof. Armstrong, Dr. Atkinson, Mr. W. Baily, Prof. Glazebrook, Mr. E. H. Griffiths, Mr. S. Lupton, Prof. Perry, Mr. Swinburne, Prof. Threlfall, and Mr. J. Walker.

Mr. ADDENBROOKE asked if the Proceedings of the Society could be published with less delay.

The CHAIRMAN promised to try and have them printed sooner.

Prof. LODGE then delivered his Presidential Address on "*The Controversy Concerning Volta's Contact Force.*"

Those who take a metallic view of the Volta contact force are accustomed to deny that the Peltier evolution of heat measures the local E.M.F. existing at a junction; they assert that it measures the rate at which that same E.M.F. varies with temperature. In the thermodynamic equation connecting the Peltier effect with the variation of *E*. with temperature, the *E*. which varies is not necessarily that at the junction considered, but is the total E.M.F. of the circuit. The reversible heat at a specified junction is a measure of the metallic E.M.F. located there. Those who say it is a temperature variation of the E.M.F. beg the question by locating the whole E.M.F. of the circuit at the particular junction they are considering; usually an interface of zinc and copper. At a chemical junction the E.M.F. is not purely thermal, and hence is not measured by the Peltier effect; it is chiefly of chemical origin, and is calculable from the energy of combination of the materials on either side of the boundary. At a metallic junction there is no such chemical potentiality. A strong current may be passed across a zinc-copper junction for years and no brass is formed. It is therefore improbable that the chemical affinity of zinc for copper is the propelling influence which causes the E.M.F. located at such a junction. In showing the volta effect experimentally a trace of liquid can act detrimentally by forming a conducting bridge between the plates, across which the bulk of the electricity passes as the metals are

being separated. The safest and clearest mode of expressing the Volta effect is that it consists in an opposite charge acquired by dry zinc and copper, while in metallic contact a charge which results from an E.M.F. of fixed value and is controlled solely by this E.M.F. and electrostatic capacity. It is undeniable that the order of the Volta force can be calculated from the differential heats of combination of the metals for oxygen, although it is doubtful whether it can be calculated from the heat of formation of brass. The opposing sides of the old controversy used to be called contact theorists and chemical theorists. Now the opposite sides are involved both in contact and both in chemical views. It is a question of which of several contacts is the effective one and what kind of chemical action or affinity is the active cause. Is it the contact and chemical affinity across the metal-metal junctions, or across the metal-air junctions? The opposite sides are thus metallic and dielectric. The metal-air force is of the order volts, the metal-metal force is of the order milli-volts.

When a piece of zinc is put in contact with a piece of copper the oxygen atoms which surround these bodies move slightly away from the copper and approach slightly nearer to the zinc. These slight motions produce the whole Volta effect. All that is necessary for the Volta effect is the inherent film on the surface, all the rest of the gas is mere dielectric, and might be substituted by a vacuum.

It was proposed by Prof. PERRY and seconded by Prof. ARMSTRONG that a meeting should be held to discuss the Address.

The meeting then adjourned until February 23rd.

NOTICES OF BOOKS.

The Early Metallurgy of Copper, Tin, and Iron in Europe; as Illustrated by Ancient Remains, and the Primitive Processes Surviving in Japan. By W. GOWLAND, F.S.A., F.C.S. London: J. B. Nichols and Sons. 1899. Pp. 56.

ALTHOUGH the primitive processes by which metals were extracted from their ores are generally dying out, they have a certain interest on account of their efficiency in spite of the rudeness of the appliances employed. The processes were, in principle, almost identical with those now in use; it is only the form of apparatus that has changed.

These ancient processes can be best studied in Japan, where, owing to the great conservatism and seclusion observed by that country until quite recently, they are (or were in 1872), still to be found in practical use. There are a number of quaint illustrations, showing the Japanese at work in their primitive ways of mining, baling water out of the mine, smelting, roasting, casting, &c., and comparing these methods with remains of ancient mining to be found in some parts of Great Britain, it is evident that those processes now in use in Japan are identical with those used in this country in prehistoric times.

The book makes interesting reading; one of the most striking thoughts to which it gives rise is, what remarkably cheap labour was to be obtained in those times.

Instruction in the Preparation of Chemical Compounds. ("Anleitung zur Darstellung Chemischer Präparate"). By Prof. Dr. H. ERDMANN. Second edition, with 15 illustrations in the text. Frankfurt-a-M.: H. Bechhold. 1899. Pp. 92.

THE object of this volume is to provide a text-book of practical instruction in the preparation of the inorganic compounds most frequently met with.

Thirty-five of the more common elements are dealt with, and details of the preparation of four or five com-

pounds of each are given. The tables at the end include a list of 75 elements with their atomic weights on two scales, viz., H=1, and O=16; as well as a register of authorities quoted, and a comprehensive index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 4, January 22, 1900.

Metallic Borates.—L. Ouvrard.—Metallic borates are difficult to prepare. The author uses the following property for their preparation:—When boric anhydride acts on melted metallic chlorides, the chlorinated compounds are only formed to a very slight degree, still less in the case of the fluorides. The double fluorides of the metals with the alkalis are used as they are soluble and more easily fusible. Cadmium borate was one of the first the author prepared. Equimolecular parts of fluorhydrate of potassium fluoride and boric anhydride, to which was added a molecule of cadmium oxide, were placed in a platinum crucible. These were heated together for some time and then fused. Boron fluoride was evolved. When all the gas was given off and the whole was in tranquil fusion, it is allowed to cool slowly and taken up with water. Needles of tri-cadmium borate were left; these crystals are insoluble in water, but easily soluble in dilute acids. Analysis shows them to have the formula $B_2O_3 \cdot 3CdO$.

New Method of Estimating Aluminium.—Alfred Stock.—When a mixture of iodide and iodate of potassium acts upon a solution of an aluminium salt, aluminium hydrate is precipitated and the corresponding quantity of iodine is liberated, according to the equation $Al(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3H_2SO_4 + 6I$. This is a reaction which begins very rapidly in the cold, but which is not complete for several days, especially with dilute solutions; the velocity of the reaction can, however, be accelerated if the iodine liberated during the reaction is removed by means of sodium thiosulphate, or by allowing the precipitation to take place when hot. By working on a boiling water-bath, the reaction is complete in a few minutes, and by removing the iodine at the same time by means of standard thiosulphate solution, a method of estimating aluminium can be devised—the precipitation being total, even in dilute solution.

MISCELLANEOUS

Formation of Hydrocyanic Acid by the Action of Carbonic Acid on Ferrocyanide of Potassium.—Guido Gigli.—If we pass a current of carbonic acid through a cold solution of ferrocyanide of potassium, there is no apparent effect; but if the solution is then submitted to distillation, it becomes cloudy as soon as the boiling point is reached, and we observe that the filtered liquid contains hydrocyanic acid. A fresh current of carbonic acid through the cloudy solution produces no effect, but if it is filtered the clear filtrate will then behave in the same manner as the original solution. This cycle of operations, action of carbonic acid gas, boiling, filtration, and cooling, can be repeated a large number of times; and the quantity of ferrocyanide decomposed or of hydrocyanic acid produced in each operation is extremely small, but sufficient to interfere with the use of carbonic acid as a means for the detection of cyanide of potassium in the ferrocyanide (Fresenius's method). The greenish precipitate which is formed seems to be the product known under the name of "Everett's white salt."—*Chemiker Zeitung*, xxii., 775.

Preparation and Reduction of Dehydromucic Acid.—H. B. Hill.—The author easily obtained dehydromucic acid with a return of about 27 per cent, by heating saccharate of potash with four times its weight of hydrobromic acid ($d=1.49$), for ten hours in a flask fitted with a vertical condenser. The dehydromucic acid is then isolated by means of the calcium salt. The reduction of this acid furnishes two products, already described by M. Seelig, and which unite with bromine, giving the well crystallised compounds answering to the formulæ, $C_6H_5Br_2O_5 \cdot H_2O$ (fusible at 145°), and $C_6H_5Br_2O_5 \cdot 2H_2O$ (fusible at 207°).—*Berichte der D. Ch. Ges.*, xxxii., p. 1221.

Hydracinnamoïn.—J. Thiele.—On reducing cinnamic aldehyde by means of zinc powder copper-plated with a solution of sulphate of copper, the author obtained hydracinnamoïn $C_6H_5 \cdot CH:CH \cdot CH(OH)CH(OH)CH:CH \cdot C_6H_5$, which crystallises in white needles, difficultly soluble in alcohol and ether, fusible at $153-154^\circ$. Hydrocinnamoïn reduces permanganate; in acetic solution it takes up bromine; heated with acids, or above its fusion point, it gives resins the same as when it is treated with an alcoholic solution of potash. It is with difficulty attacked by acetic anhydride. Dissolved in pyridine it furnishes, by the action of chloride of acetyl, a diacetate which crystallises in alcohol in small white prisms, fusible at $118-119^\circ$. Its dibenzoate, prepared in an analogous manner, occurs in fine colourless needles, fusible at $169-170^\circ$.—*Berichte der D. Ch. Ges.*, xxxii., p. 1296.

On the Peroxysulphate of Silver.—E. Mulder.—The electrolysis of sulphate of silver offers great difficulties on account of the very slight solubility of this salt, and further, it is necessary to operate in very dilute solutions ($\frac{1}{4}$ saturated), and to eliminate the SO_4H_2 formed, which tends to cause a reverse action. This last proviso is effected by continuous neutralisation by means of carbonate of silver, with the help of an automatic arrangement driven by clock-work. We thus obtain a microcrystalline compound, the peroxysulphate of silver, which is decomposed by warm water, with the precipitation of Ag_2O_2 , disengagement of oxygen, and formation of sulphate of silver. This body is thus analogous to the peroxynitrate of silver, and can be represented by the formula $5Ag_2O_2 \cdot (SO_4)_3O \cdot Ag_2$; it decomposes under the influence of sulphuric acid, and even spontaneously.—*Rev. d. Trav. Ch. P. B.*, xviii., p. 91.

An Ammonical Derivative of Fructose.—C. A. Lobry de Bruyn.—This derivative is obtained by dissolving 100 to 150 grms. of levulose in 100 c.c. of methylic alcohol saturated with ammonia, and leaving the solution to stand by itself, in contact with the air for several weeks. The product of the reaction is deposited in the form of amorphous grains, or crystalline leaves; the return is about 20 grms. for the above-mentioned quantities. It is purified by re-crystallising in water. The formation of this ammonical derivative takes place according to the equation, $C_6H_{12}O_6 + NH_3 = C_6H_9NO_4 + 2H_2O + H_2$; $\alpha_D = -75^\circ$. This body is not basic, and its stability is much greater than that of the osamines; it does not give osazone, but reduces Fehling's solution warm, and is not attacked by nitrous acid. It is reduced by sodium amalgam. When treated with acetic anhydride and acetate of sodium, a tetracetate is obtained which crystallises in white flakes, fusible at 174° , $\alpha_D = -6.7^\circ$, in chloroform solution at 2.4 per cent.—*Berichte*, xviii., 71.

Measurement of Solubilities at Various Temperatures.—B. Pawlewski.—The author proposes using a small piece of apparatus, formed of two vessels A and B, each fitted with a cork having two holes, and communicating one with the other by means of a syphon with a filtering plug, and with the outer air by two vertical tubes; the whole is plunged into a bath at a constant temperature. A is a test-tube containing the substance and its solvent; agitation is caused by blowing from B to A through one of the vertical tubes. When saturation is reached, we blow in the opposition direction; a certain

quantity of the saturated solution then passes into B, which is a conical flask. The whole apparatus is then withdrawn from the bath, and B is weighed. The vertical tubes are fitted with condensers, for cases in which the solvents are very volatile. The author gives as an example the determination of the solubility of chlorate of potassium in water. The following is an extract from the table:—

Temperature.	Weight of salt in 100 c.c. of saturated solu- tion.	Weight of salt dissolved in 100 c.c. of water.	No. of parts of water to dis- solve 1 part of salt.
0°	3.06	3.14	31.8
15°	5.11	5.35	18.5
50°	15.18	17.95	5.6
100°	35.83	55.54	1.8

—*Berichte*, xxxii., p. 1040.

Analysis of some Commercial Samples of Carbide of Calcium.—Henri Moissan.—Since the first publication of the preparation of crystallised carbide of calcium by means of the electric furnace, this substance has become of industrial importance, and a certain amount of difficulty is experienced in making it by the ton. A great deal of care is necessary in the preparation of the charge, and the behaviour of the large electrodes which have to carry such intense currents, &c. The disposal of, or utilisation of, the enormous amount of incandescent gases has also offered some difficulty. Carbide of calcium can now, however, be produced of a much better quality than formerly, but it is still of advantage to have it analysed. Theoretically, 1 grm. of carbide of calcium should give 349 litres of acetylene gas; but on decomposing a few samples with milk of lime, previously saturated with acetylene gas, the following volumes were obtained, reduced to 0° and 760 m.m.:— $V = 292.80$, 294.10 , 301.30 , 304.61 , 307.72 , 316.41 , 318.77 . If the carbide of calcium has not got a melted crystalline appearance the return of gas is much less, 228.60, 250.40, 260.30 for instance. The author has more particularly studied the insoluble residue left by the action of water on carbide of calcium. To render this more easy, the carbide was decomposed by sugar-water so as to keep the lime in solution as sucrate of lime. The residue was filtered and washed, then treated with alcohol, and finally with ether, and dried in vacuo at 40°. It consists principally of silicide of carbon, silicide of calcium and iron, and sometimes a little sulphide of calcium and graphite. Taken up with dilute HCl it loses a little weight, and iron, lime, alumina, and phosphorus is found in solution. The silicide of carbon and the graphite remain unattacked, and the sulphide of calcium has disappeared. By this treatment, and examining the residues under the microscope, the form in which most of the impurities exist was determined.—*Bull. de la Soc. Chim. de Paris*, Series 3, xxi., Nos. 20—21.

MEETINGS FOR THE WEEK.

- TUESDAY, 20th.**—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester.
WEDNESDAY, 21st.—Society of Arts, 8. "Artistic Copyright," by Edwin Bale.
— Microscopical, 8. Exhibition of Photo-micrographic and Projection Apparatus (with Lantern Illustrations), by J. W. Measures.
— Institution of Mining and Metallurgy, 8. "On the Development of Silver Smelting in Mexico," by Otto H. Hahn. "Segregation of Mine Accounts," by W. B. Middleton. "Notes on a Novel Association of Gold," by H. F. Collins.
THURSDAY, 22nd.—Royal Institution, 3. "Modern Astronomy," by Prof. H. H. Turner, M.A., F.R.S.
FRIDAY, 23rd.—Royal Institution, 9. "Recent Studies in Gravitation," by John H. Poynting, D.Sc., F.R.S.
— Physical, 5. Prof. R. W. Wood, of the University of Wisconsin, will Exhibit and Describe his:—(1) Photographs of Sound Waves and the Kinematographical Demonstration of the Evolutions of Reflected Wave-fronts; (2) A New Pseudoscope; (3) Diffraction Colour Photographs; (4) Artificial Parhelia.
SATURDAY, 24th.—Royal Institution, 3. "The Idea of Tragedy in Ancient and in Modern Drama," by W. L. Courtney, M.A., LL.D.

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MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

LENT TERM.—Monday, January 8, to Saturday, Apr. 7.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2100.

ON THE VISCOSITY OF ARGON AS AFFECTED BY TEMPERATURE.*

By Lord RAYLEIGH, F.R.S.

ACCORDING to the kinetic theory, as developed by Maxwell, the viscosity of a gas is independent of its density, whatever may be the character of the encounters taking place between the molecules. In the typical case of a gas subject to a uniform shearing motion, we may suppose that of the three component velocities v and w vanish, while u is a linear function of y , independent of x and z . If μ be the viscosity, the force transmitted tangentially across unit of area perpendicular to y is measured by $\mu du/dy$. This represents the relative momentum, parallel to x , which in unit of time crosses the area in one direction, the area being supposed to move with the velocity of the fluid at the place in question. We may suppose, for the sake of simplicity, and without real loss of generality, that u is zero at the plane. The momentum, which may now be reckoned absolutely, does not vanish, as in the case of a gas at rest throughout, because the molecules come from a greater or less distance, where (*s.g.*), the value of u is positive. The distance from which (upon the average) the molecules may be supposed to have come depends upon circumstances. If, for example, the molecules, retaining their number and velocity, interfere less with each other's motion, the distance in question will be increased. The same effect will be produced, without a change of quality, by a simple reduction in the number of molecules, *i.e.*, in the density of the gas, and is not difficult to recognise that the distance from which the molecules may be supposed to have come is *inversely as the density*. On this account the passage of tangential momentum *per molecule* is *inversely as the density*, and since the number of molecules crossing is directly as the density, the two effects compensate, and upon the whole the tangential force, and therefore the viscosity, remain unaltered by a change of density.

On the other hand, the manner in which this viscosity varies with temperature depends upon the nature of the encounters. If the molecules behave like Boscovich points, which exercise no force upon one another until the distance falls to a certain value, and which then repel one another infinitely (erroneously called the theory of elastic spheres), then, as Maxwell proved, the viscosity would be proportional to the square root of the absolute temperature. Or again, if the law of repulsion were as the inverse fifth power of the distance, viscosity would be as the absolute temperature.

In the more general case where the repulsive force varies as r^{-n} , the dependence of μ upon temperature may also be given. If v be the velocity of mean square proportional to the square root of the temperature, μ varies as—

$$\frac{n+3}{v^{n-1}},$$

a formula which includes the cases ($n=5, n=\infty$) already specified. If we assume the law already discussed—that μ is independent of density—this conclusion may be arrived at very simply by the method of “dimensions.”

In order to see this we note that the only quantities (besides the density) on which μ can depend are m the mass of a particle, v the velocity of mean square, and k

the repulsive force at unit distance. The dimensions of these quantities are as follows:—

$$\begin{aligned}\mu &= (\text{mass})^1 (\text{length})^{-1} (\text{time})^{-1}, \\ m &= (\text{mass})^1, \\ v &= (\text{length})^1 (\text{time})^{-1}, \\ k &= (\text{mass})^1 (\text{length})^{n+1} (\text{time})^{-n}.\end{aligned}$$

Thus, if we assume—

$$\mu \propto m^x \cdot v^y \cdot k^z \quad \dots \dots \dots (1),$$

we have—

$$1 = x + z, \quad -1 = y + (n+1)z, \quad -1 = -y - 2z,$$

whence—

$$x = \frac{n+1}{n-1}, \quad y = \frac{n+3}{n-1}, \quad z = \frac{2}{n-1}.$$

Accordingly—

$$\mu = a \cdot m^{\frac{n+1}{n-1}} \cdot v^{\frac{n+3}{n-1}} \cdot k^{\frac{2}{n-1}} \dots \dots \dots (2),$$

where a is a purely numerical coefficient. For a given kind of molecule, m and k are constant. Thus—

$$\mu \propto v^{\frac{n+3}{n-1}} \propto \theta^{\frac{n+3}{n-2}} \dots \dots \dots (3).$$

The case of sudden impacts ($n=\infty$) gives, as already remarked, $\mu \propto \theta^{1/2}$. Hence k disappears, and the consideration of dimensions shows that $\mu \propto d^{-3}$, where d is the diameter of the particles.

The best experiments on air show that, so far as a formula of this kind can represent the facts, $\mu \propto \theta^{0.77}$. It may be observed that $n=8$ corresponds to $\mu \propto \theta^{0.70}$.

When we remember that the principal gases, such as oxygen, hydrogen, and nitrogen, are regarded as diatomic, we may be inclined to attribute the want of simplicity in the law connecting viscosity and temperature to the complication introduced by the want of symmetry in the molecules and consequent diversities of presentation in an encounter. It was with this idea that I thought it would be interesting to examine the influence of temperature upon the viscosity of argon, which in the matter of specific heat behaves as if composed of single atoms. From the fact that no appreciable part of the total energy is rotatory, we may infer that the forces called into play during our encounter are of a symmetrical character. It seemed therefore more likely that a simple relation between viscosity and temperature would obtain in the case of argon than in the case of the “diatomic” gases.

The best experimental arrangement for examining this question is probably that of Holman (*Phil. Mag.*, 1877, iii., p. 81), in which the same constant stream of gas passes in succession through two capillaries at different temperatures, the pressures being determined before the first and after the second passage, as well as between the two. But to a gas like argon, available in small quantities only, the application of this method is difficult. And it seemed unnecessary to insist upon the use of constant pressures, seeing that it was not proposed to investigate experimentally the dependence of transpiration upon pressure.

The theoretical formula for the volume of gas transpired, analogous to that first given by Stokes for an incompressible fluid, was developed by O. E. Meyer (*Pogg. Ann.*, 1866, cxxvii., p. 269). Although not quite rigorous, it probably suffices for the purpose in hand. If p_1, V_1 denote the pressure and volume of the gas as it enters the capillary, p_2, V_2 as it leaves the capillary, we have—

$$p_1 V_1 = p_2 V_2 = \frac{\pi t R^4}{16 \mu l} (p_1^2 - p_2^2) \dots \dots \dots (4).$$

In this equation t denotes the time of transpiration, R the radius of the tube, l its length, and μ the viscosity measured in the usual way.

In order to understand the application of the formula for our present purpose it will be simplest to consider first the passage of equal volumes of different gases

* A Paper read before the Royal Society, January 18, 1900.

through the capillary, the initial pressures, and the constant temperature being the same. In an apparatus, such as that about to be described, the pressures change as the gas flows, but if the pressures are definite functions of the amount of gas which at any moment has passed the capillary, this variation does not interfere with the proportionality between t and μ . For example, if the viscosity be doubled, the flow takes place precisely as before, except that the scale of time is doubled. It will take twice as long as before to pass the same quantity of gas.

Although different gases have been employed in the present experiments, there has been no attempt to compare their viscosities, and indeed such a comparison would be difficult to carry out by this method. The question has been, how is the viscosity of a given gas affected by a change of temperature? In one set of experiments the capillary is at the temperature of the room; in a closely following set the capillary is bathed in saturated steam at a temperature that can be calculated from the height of the barometer.

If the temperature were changed throughout the whole apparatus from one absolute temperature θ to another absolute temperature θ' , we could make immediate application of (4); the viscosities (μ , μ') at the two temperatures would be directly as the times of transpiration (t , t'). The matter is not quite so simple when, as in these experiments, the change of temperature takes place only in the capillary. A rise of temperature in the capillary now acts in two ways. Not only does it change the viscosity, but it increases the volume of gas which has to pass. The ratio of volumes is θ' , θ ; and thus—

$$\frac{\mu'}{\mu} = \frac{t'}{t} \times \frac{\theta}{\theta'} \quad \dots \dots \dots (5),$$

subject to a small correction for the effect of temperature upon the dimensions of the capillary. It is assumed that the temperature of the reservoirs is the same in both transpirations.

The apparatus is shown Fig. 1. The gas flows to and fro between the bulbs A and B, the flow from A to B only being timed. It is confined by mercury, which can pass through U connections of blown glass from A to C and from B to D. The bulbs B, C, D are supported upon their seats with a little plaster-of-paris. The capillary is nearly 5 feet (150 c.m.) in length, and is connected with the bulbs by gas tubing of moderate diameter, all joints being blown. E represents the jacket through which steam can be passed; its length exceeds that of the capillary by a few inches.

In order to charge the apparatus, the first step is the exhaustion. This is effected through the tap F, with the aid of a Toppler pump, and it is necessary to make a corresponding exhaustion in C and D, or the mercury would be drawn over. To this end the rubber terminal H is temporarily connected with C, while I leads to a common air-pump. When the exhaustion is complete, the gas to be tried is admitted gradually at F, the atmosphere being allowed again to exert its pressure in C and D. When the charge is sufficient, F is turned off, after which G remains open to the atmosphere, and H is connected to a manometer.

When a measurement is commenced, the first step is to read the temperatures of the bulbs and of the capillary; I is then connected to a force pump, and pressure is applied until so much of the gas is driven over that the mercury below A and in B assumes the positions shown in the diagram. I is then suddenly released so that the atmospheric pressure asserts itself in D, and the gas begins to flow back into B. The bulb J allows the flow a short time in which to establish itself before the time measurement begins as the mercury passes the connection passage K. When the mercury reaches L, the time measurement is closed.

One of the points to be kept in view in designing the apparatus is to secure long enough time of transpiration

without unduly lowering the driving pressure. At the beginning of the measured transpiration the pressure in A was about 30 c.m. of mercury above atmosphere, and that in B about 2 c.m. below atmosphere. At the end the pressure in A was 20 c.m., and in B 3 c.m., both above atmosphere. Accordingly the driving pressure fell from 32 to 17 c.m.

Three, or, in the case of hydrogen, five, observations of the time were usually taken, and the agreement was such as to indicate that the mean would be correct to perhaps one-tenth of a second. The time for air at the temperature of the room was about ninety seconds, and for hydrogen forty-four seconds, but these numbers are not strictly comparable.

When the low temperature observations were finished, the gas was lighted under a small boiler placed upon a shelf above the apparatus, and steam was passed through the jacket. It was necessary to see that there was enough heat to maintain a steady issue of steam, yet not so much as to risk a sensible back pressure in the jacket. The time of transpiration for air was now about 139 seconds. Care was always taken to maintain the temperature of the bulbs at the same point as in the first observations.

There are one or two matters as to which an apparatus on these lines is necessarily somewhat imperfect. In the high temperature measurements the whole of the gas in the capillary is assumed to be at the temperature of boiling water, and all that is not in the capillary to be at the temperature of the room, assumptions not strictly compatible. The compromise adopted was to enclose in the jacket the whole of the capillary and about 2 inches at each end of the approaches, and seems sufficient to exclude sensible error when we remember the rapidity with which heat is conducted in small spaces. A second weak point is the assumption that the instantaneous pressures are represented by the heights of the moving mercury columns. If the connecting U-tubes are too narrow, the resistance to the flow of mercury enters into the question in much the same way as the flow of gas in the capillary. In order to obtain a check upon this source of error the apparatus has been varied. In an earlier form the connecting U-tubes were comparatively narrow; but the result for the ratio of viscosities of hot and cold air was substantially the same as that subsequently obtained with the improved apparatus, in which these tubes were much widened. Even if there be a sensible residual error arising from this cause, it can hardly affect the comparison of temperature-coefficients of gases whose viscosity is nearly the same.

I will now give an example in detail from the observations of December 21 with purified argon. The times of transpiration at the temperature of the room (15° C.) were in seconds—

$$104\frac{1}{2}, 104\frac{1}{2}, 104\frac{1}{2}. \text{ Mean, } 104\cdot67.$$

When the capillaries were bathed in steam, the corresponding times were—

$$167\frac{1}{2}, 167\frac{1}{2}, 167\frac{1}{2}. \text{ Mean, } 167\cdot58.$$

The barometer reading (corrected) being 767·4 m.m., we deduce as the temperature of the jacket 100·27° C. Thus $\theta = 287\cdot5$, $\theta' = 372\cdot8$. The reduction was effected by assuming—

$$\frac{t'}{t} = \left(\frac{\theta'}{\theta} \right)^x \quad \dots \dots \dots (6).$$

With the above values we get—

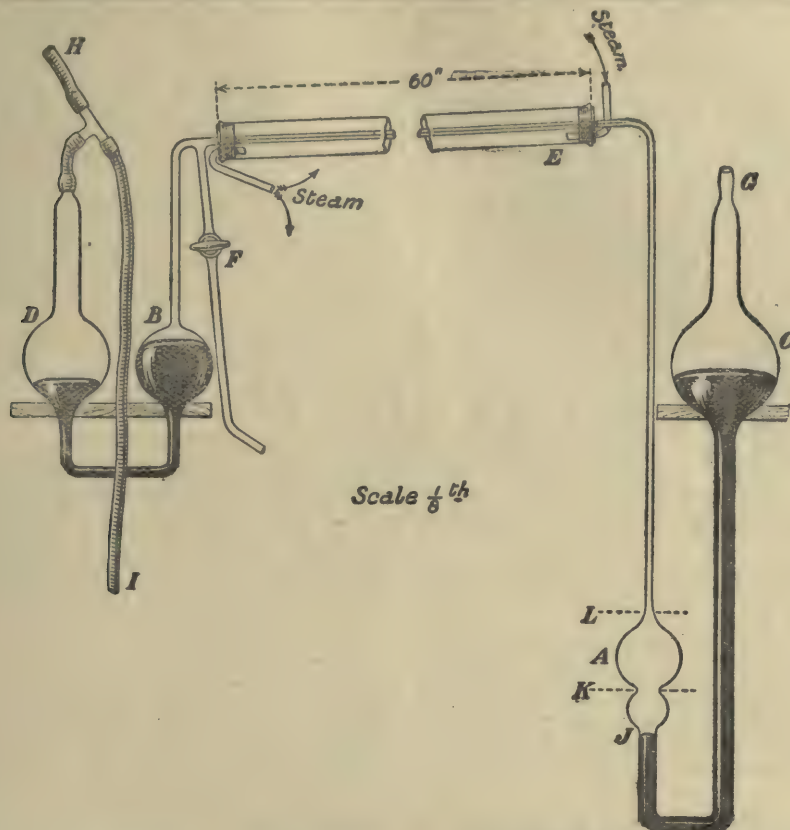
$$x = 1\cdot812.$$

As appears from (5), the integral part of x relates merely to the expansion of the gas by temperature. If we take—

$$\frac{\mu'}{\mu} = \left(\frac{\theta'}{\theta} \right)^n \quad \dots \dots \dots (7),$$

we get—

$$n = 0\cdot812.$$



This number is, however, subject to a small correction for the expansion of the glass of the capillary. As appears from (4), the ratio μ' , μ as used above requires to be altered in the same ratio as that in which the glass expands by volume. The value of n must accordingly be increased by 0.010, making—

$$n = 0.822.$$

The following table embodies the results obtained in a somewhat extended series of observations. The numbers given are the values of n in (7), corrected for the expansion of the glass:—

Air (dry)	0.754
Oxygen	0.782
Hydrogen	0.681
Argon (impure)	0.801
Argon (best)	0.815

In the last trials, the argon was probably within 1 or 2 per cent of absolute purity. The nitrogen lines could no longer be seen, and scarcely any further attraction could be effected on sparking with oxygen or hydrogen.

It will be seen that the temperature change of viscosity in argon does not differ very greatly from the corresponding change in air and oxygen. At any rate the simpler conditions under which we may suppose the collisions to occur, do not lead to values of n such as 0.5, or 1.0, discussed by theoretical writers.

I may recall that on a former occasion (*Roy. Soc. Proc.*, January, 1896) I found the viscosity of argon to be 1.21 relatively to that of air, both being observed at the temperature of the room.

Chemical Society.—An extra Meeting of the Society will be held on Thursday, March 8th, when a Lecture "On Recent Researches on Nitrification" will be given by Professor Warington, F.R.S. The Chair will be taken at 8.30 p.m.

THE PREPARATION AND PROPERTIES OF CRYSTALLISED PHOSPHIDE OF CALCIUM.

By HENRI MOISSAN.

By allowing the vapour of phosphorus to react on lime heated to redness, Paul Thenard obtained an amorphous product of a cinnabar-red colour, the composition of which answered to the formula P_2CaO (P. Thenard, *Ann. Chim. Phys.*, 1895, xiv., 12). This new body, which he called phosphide of lime, decomposed in the presence of water, and the reaction enabled him to establish the existence and the properties of the different hydrides of phosphorus. Previously to this, Dulong had described a general method for the preparation of phosphides by the action of the vapour of phosphorus on the metal. These experiments were repeated by Vigier.

This latter process was only applicable to the preparation of phosphide of calcium on the condition of the metal being pure, which had not been achieved before our researches on the subject.

Preparation of Crystallised Phosphide of Calcium by the Electric Furnace.

Phosphide of calcium can be prepared in the electric furnace, by the reduction of tricalcic phosphate by means of carbon. This operation, however, requires certain precautions, on account of the relatively easy decomposition of phosphide of calcium at the high temperature of the electric furnace.

We first prepared pure tricalcic phosphate by precipitation. This compound, after desiccation, was calcined in a Perrot furnace, then reduced to a fine powder, and finally mixed with carbon in the following proportions:—

Tricalcic phosphate	310 parts
Lamp-black	96 "

A small quantity of essence of turpentine was added to this mixture, so that it could be moulded into small cylinders, under pressure. These were then calcined in the Perrot furnace in a crucible brasqued with lamp-black.

The intimate mixture of phosphate of calcium and carbon is then placed in the crucible of the electric furnace and submitted to the action of an arc of 590 ampères and 45 volts, for four minutes.

On cooling, the melted mass is withdrawn from the crucible; it should not adhere to the sides, and will only do so when the heating has been carried on too long. In such a case the mass of phosphide of calcium will be contaminated round the edges with a small quantity of carbide of calcium. If, on the other hand, the heating has been insufficient, the phosphide will be mixed with melted un-reduced phosphate, in the midst of which can be plainly distinguished the red crystals of the phosphide.

During this operation in the electric furnace only a very small quantity of phosphorus vapours is given off. But if we continue heating after the reduction is complete, the phosphide of calcium formed is in its turn decomposed, the phosphorus is distilled in abundance, and its vapour burns on escaping from the furnace. Finally, the calcium unites with the carbon, and there only remains carbide of calcium, which contains but a very small quantity of phosphorus.

Thus, as we remarked above, when we wish to obtain pure phosphide of calcium by this method, it is important not to continue the heating for too long.

We can also obtain fused phosphide of calcium, by heating, in a carbon crucible in the electric furnace, P. Thenard's phosphide of lime, prepared by the action of a large excess of phosphorus vapour on lime kept at a red heat. With an arc of 800 ampères and 50 volts, fusion takes place in seven or eight minutes. A well-melted, deep red mass remains, contaminated with carbide of calcium.

Preparation of Amorphous Phosphide of Calcium, by the Direct Union of Phosphorus and Calcium.

To effect this synthesis, a Bohemian glass tube is taken, closed at one end, and at the bottom there is placed a fair quantity of well-dried red phosphorus. A porcelain boat, placed in the lower part of the tube, contains calcium in the form of small crystals. The air is exhausted from the tube, which is then heated to a dull red, where the calcium is, and over which the fumes of phosphorus soon spread. Incandescence is produced, and very soon the whole of the metal is transformed into phosphide.

This last compound has the same formula as that obtained by means of the electric furnace, as we shall show later on.

Properties.

Phosphide of calcium, whether prepared in the electric furnace or by the direct union of the two elements, has the same colour when examined under the microscope in a state of fine division. It occurs in reddish brown fragments, of which the colour approaches that of nitride of calcium. When it has been prepared in the electric furnace it has a crystalline fracture, and, further, when the reduction has not been complete, we meet with distinctly formed crystals of a deep red colour, in the middle of the melted phosphide.

Phosphide of calcium is not easy to fuse; we have only succeeded in melting it by means of the electric furnace. In the combination of phosphorus with calcium, a compound the formation of which always takes place with incandescence, we only obtain an amorphous mass.

At the temperature of softening Bohemian glass, phosphide of calcium dissociates slowly *in vacuo*. The escape of a small quantity of phosphorus vapour is very marked. The tension of dissociation only reaches a few millimetres; its density at $+15^{\circ}$ is 2.51.

At 900° phosphide of calcium is not sensibly changed in an atmosphere of hydrogen.

Chlorine does not react on phosphide of calcium at all in the cold, but it suffices to slightly raise the temperature, to about 100° for example, to start the reaction, which then proceeds with lively incandescence.

Chloride of calcium is formed, as well as fumes of chloride of phosphorus. The action of bromine is in every way comparable with the action of chlorine, and the vapour of iodine attacks this phosphide at about a dull red heat.

The combustion of phosphide of calcium in oxygen takes place towards 300° with lively incandescence, forming lime and phosphoric anhydride. Sulphur reacts in the same manner at about 300° ; the decomposition of the phosphide takes place with a considerable disengagement of heat, and the production of a yellow sublimate and formation of sulphide of calcium.

The action of nitrogen on phosphide of calcium seemed to us to be particularly interesting. In fact, if the nitrogen was able to drive the phosphorus out of this compound, we could easily pass from the phosphide to the nitride of calcium.

We have already shown that nitride of calcium is easily decomposed on contact with water, giving ammonia, a reaction susceptible of commercial application.

But the heat of formation of the phosphide of calcium appears to be higher than that of the nitride, as all our experiments up to a temperature of 900° have been fruitless. Phosphide of calcium, heated in an atmosphere of nitrogen to 900° , does not vary in weight, and does not give off any ammonia on its decomposition by water.

At 1200° nitrogen partially combines with calcium, with the separation of a small quantity of phosphorus; but the reaction is far from being complete, and the residue in the presence of water gives a mixture of ammonia and phosphoretted hydrogen, the latter being in great excess. We are here in the presence of a dissociation of phosphide of calcium.

When heated in the vapour of arsenic, at the temperature of melting glass, phosphide of calcium was not attacked. Boron and carbon are without action at a temperature of 700° . In the electric furnace it is no longer the same, and the carbon displaces the phosphorus from phosphide of calcium, producing melted carbide of calcium.

The gaseous hydracids react with energy on phosphide of calcium. Hydrochloric acid attacks it with incandescence, at a red heat. Towards 700° sulphuretted hydrogen does not attack it to any noticeable extent. It is the same with ammonia gas. The reaction of water with this body is very important. On contact with cold water phosphide of calcium is at once decomposed, with the formation of hydrate of lime and phosphoretted hydrogen gas. If the phosphide of calcium is in crystalline fragments, the hydrate of lime produced hinders the reaction; if, on the contrary, the phosphide is in powder, the reaction is violent.

When the phosphide has been sufficiently heated in the electric furnace, the phosphoretted hydrogen produced in the decomposition by water is not spontaneously inflammable on contact with the air. This new phosphide is thus very different from the body produced by P. Thenard. However, the reaction of the decomposition is still complex, and we do not obtain the whole of the phosphorus from the phosphide as phosphoretted hydrogen, PH_3 . Some samples, which were less heated, gave with water a phosphoretted hydrogen contaminated with free hydrogen. When, on the contrary, the phosphide had been carried to a very high temperature, hydrogen was no longer given off, but a small quantity of acetylene gas was collected. We shall give all the figures of these analyses in the paper we are about to publish in the *Annales de Chimie et de Physique*.

Acids will not attack this phosphide, except in respect of the water they may contain; thus, with monohydrated nitric acid, the attack is almost *nil* in the cold; when heated it is very slow. With ordinary nitric acid the

oxidation is rapid in the cold—nitrous fumes are produced as well as a spontaneously inflammable gas.

In the same way, fuming sulphuric acid does not attack phosphorus in the cold, while the decomposition is violent with dilute sulphuric acid.

Absolute alcohol, ether, benzene, and essence of turpentine do not react at the ordinary temperature.

On the other hand, oxidising agents attack with violence, both the chlorate and bichromate of potassium in fusion oxidise it with incandescence. If we gently heat a mixture of permanganate of potassium and powdered phosphide of calcium, the reaction is violent, and produces incandescence and explosion. Both the protoxide and binoxide of nitrogen oxidise it in the same manner when warmed, with lively incandescence. Lime and a very small quantity of nitride are formed.

Analysis of Phosphide of Calcium.

Phosphide of calcium was decomposed by direct oxidation by means of fuming nitric acid. The metal was precipitated in the state of sulphate of calcium in alcohol, and the phosphoric acid was then weighed in the form of ammonio-magnesium phosphate. In this manner we found the following figures:—Ca, 65·82, 65·71, 65·38, and 65·40; Ph, 33·79, 33·92, and 33·85,—theory for $\text{Ph}_2\text{Ca}_3 = \text{Ca}, 85·93; \text{Ph}, 34·06$.

These figures must be compared with those given by synthesis. The apparatus was arranged as before; the boat was weighed empty, then filled with calcium, and finally when containing the phosphide of calcium formed; the figures were:—Ca, 66·31 and 66·12; Ph, 33·53 and 33·41.

Conclusions.

To sum up, the reduction of the tricalcic phosphate by carbon gives, under certain conditions, a crystallised phosphide of calcium, of a deep red colour, answering to the formula Ph_2Ca_2 . The most curious reaction of this new compound is its easy decomposition of cold water with the formation of slaked lime and phosphoretted hydrogen.

It is of sufficient interest to justify the remark that a large number of binary compounds of calcium possess this curious property of decomposing cold water and giving a hydrated oxide, and a gaseous compound of hydrogen united to the other element of the binary compound.

Hydride of calcium decomposes cold water with the evolution of hydrogen. Carbide of calcium decomposes cold water with the evolution of acetylene. Nitride of calcium gives the same reaction with the production of ammonia. We now see that phosphide of calcium can also give phosphoretted hydrogen. Finally, M. Lebeau has only just announced that the crystallised arsenides and antimonides of calcium behave in the same manner, giving the corresponding hydrides or the products of their decomposition, if the hydrides are unstable at the temperature of the experiment. The generality of this reaction appears to be very interesting.

We would finally remark that most of these new compounds have been prepared by means of the electric furnace.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 22.

Action of Alkalis on Sugars.—C. Lobry de Bruyn and W. A. van Ekenstein.—Maltose heated to 100° with normal KOH for three hours, gives first glucose, which in its turn is transformed into mannose. The solution further contains a non-fermentable product which hydrolysed with a dilute acid forms glucose. Melibiose, like lactose, gives, under the same conditions, galactose; but no writers have been able to put forward any evidence as to the formation of glucose. There appears to be formed, as in the case of maltose, an anhydride of glucose which by hydrolysis regenerates the former.—*Revue Trav. Chem. P.-B.*, xviii., p. 147.

ON THE HEAT OF FORMATION OF QUICK-LIME FROM ITS ELEMENTS.

By HENRI MOISSAN.

THE heat of formation of quicklime from its elements, calcium and oxygen, has been determined by Thomson (*Thermochemische Untersuchungen*, vol. iii.), who found it to be +131·5 cal. But the results given by him offer several points of uncertainty, by reason of the impurities in his calcium, and also on account of the method used.

These experiments were made with calcium containing iron, attacked in the calorimeter by a solution of hydrochloric acid, and the weight of the calcium was deduced from the volume of hydrogen given off. Further, the operation was carried out in the presence of petroleum, which necessarily complicated the experiment.

We came to the conclusion that it was indispensable to repeat this determination with the pure metal which was prepared by the help of its solubility in sodium. For these experiments, we used the calorimeter and the methods described by M. Berthelot.

When calcium, obtained in small crystals, is thrown on to the surface of water, it decomposes this latter very rapidly, and if the quantity of water is not very great, or if the calcium is in the form of fine powder, incandescent phenomena may take place. Further, each particle of calcium becomes surrounded with a cushion of hydrogen, and runs about on the surface of the liquid. It is therefore impossible, under the circumstances, to make any thermometric determination. On the other hand, if the metal is melted, or agglomerated by pressure, the decomposition on contact with water will be much slower, on account of the slaked lime which quickly encases the metal and retards the reaction.

A cylinder of calcium weighing about 1 grm. sometimes requires more than an hour's contact with water to become transformed into slaked lime, and the experiment is much too long to be applied to a calorimetric measurement.

To prevent these drawbacks we endeavoured to make only slightly agglomerated—that is to say, porous—cylinders, the transformation of which in the presence of water would not take more than three or four minutes.

But in these new experiments, as soon as the height of the cylinder was more than one-third of its diameter, the compression was no longer uniform, and the metal became disaggregated during the attack by water; small particles became detached and ran about the surface of the liquid.

Finally, the preparation of the cylinder always necessitated a more or less prolonged handling of the calcium in the presence of air, which may give rise to a superficial oxidation with the formation of a small quantity of slaked lime.

We finally adopted the following method of procedure:—

Pure calcium in small crystals is placed in a cylindrical platinum tube, 0·04 metre long and 0·01 metre in diameter, formed of two parts fitting tightly one in the other. This tube is pierced with a large number of small holes of about 0·25 m.m. in diameter. When this platinum cylinder is thrown into water a very small quantity of liquid penetrates the interior, and the disengagement of hydrogen which takes place immediately prevents the admission of any more water. For this reason the decomposition is never too violent, and the reaction can be regulated with ease.

In the preliminary experiments we found that 1 grm. of calcium was completely attacked in three or four minutes. At the end of this time not a trace of unoxidised metal remained inside the platinum cylinder. At the end of the experiment the water became milky, and contained slaked lime in suspension, which indicated a complete saturation of this base.

To get the temperature of the calcium in equilibrium with that of the water in the calorimeter, the platinum

tube was placed in a tube of very thin glass of slightly greater volume, sealed before the blowpipe, and kept for a whole night at the bottom of the calorimeter filled with water. The next morning the glass tube was broken at the moment of commencing the experiment, and the variations of temperature then noted.

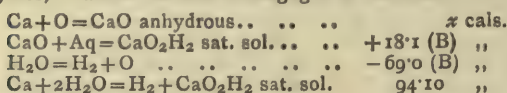
The weight of the calcium used was determined in two different manners:—

1. By weighing it in its natural state.
2. By estimation in the state of lime at the termination of the experiment. These two determinations give very close results.

It should be added that all the manipulation of the calcium, for filling the cylinder, should be performed at the bottom of a large glass vessel filled with dry carbonic acid gas.

In this manner we obtained for the reaction, $\text{Ca} + 2\text{H}_2\text{O} = \text{H}_2 + \text{CaO}_2\text{H}_2$, saturated solution, in two successive experiments, 94.74 cal. and 93.44 cal.; which gives a mean of 94.10 cal.

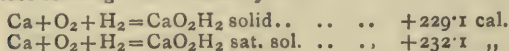
From this it is easy to calculate the heat of formation of lime from its elements by means of the two following cycles, in which the heat disengaged is the same:—



from which we get—

$$\begin{aligned} x + 18.1 - 69 &= 94.10 \text{ cal.} \\ x &= 145.0 " \end{aligned}$$

a figure which is decidedly higher than that obtained by Thomson. From this figure we can immediately calculate those relating to the calcic hydrate:—



We must explain that, according to these experiments, the heat of formation of the lime is greater than that of the oxides of potassium (+98.2), and of sodium (+100.9), which establishes the fact that calcium ought to displace sodium and potassium from their oxides; this actually occurs, as we have already shown when dealing with the chemical properties of calcium (*Comptes Rendus*, cxxvii., p. 584).

If we look over the heats of formation of the different oxides (Berthelot, *Thermochimie*, i., p. 710), we see that lithia, Li_2O , gives off +141.2 cal., in its production from its elements; although this figure is very close to that of quicklime, still it is lower.

We therefore thought it would be of interest to attempt to replace the lithium in lithia by metallic calcium. We did not, however, forget that we ought not, without certain reservations, to apply the results obtained at the ordinary temperature to reactions produced at a red heat in the dry way.

The experiment was performed in the following manner: A mixture of anhydrous lithia and crystals of calcium was placed in a tube of combustion glass. The air was exhausted by means of a Sprengel pump, and the mixture heated; the reaction took place at a dull red heat without incandescence, and the brilliant lithium ring was seen to condense on the cool part of the glass tube. Thus, as foreseen by theory, calcium displaces lithium from its anhydrous oxide.

If we consider the heats of formation of other oxides, we notice that $\text{Mg} + \text{O} = 143.4 \text{ cal.}$; it would here again appear that calcium ought to displace the magnesium. Now, this is not the case; we heated a mixture of quicklime and powdered magnesium in an iron crucible with a screw stopper, in the presence of an excess of sodium. This latter metal has the property, as we have already shown, of dissolving calcium when heated.

After having heated the mixture to redness for a few instants, the cake of sodium, which is found in the upper part of the crucible after cooling, contained crystals of

calcium easily separated by means of anhydrous alcohol. Winkler's experiments have already made this known (*Berichte*, 1890, p. 122).

To sum up, magnesium easily displaces calcium from quicklime at a red heat.

We thought that the interpretation of this experiment might lead to the opinion that the heat of formation of anhydrous magnesia, determined by Thomson (*Thermochemische Untersuchungen*, iii., p. 241), was a little low.

At the period when M. Thomson made these determinations, metallic magnesium was not prepared in a great state of purity.

There would therefore be nothing surprising if this experiment had given a calorific value some units lower than the true figure.

We shall continue the study of this determination.—*Bull. Soc. Chim.*, Series 3, xxi., No. 22.

ON NICKEL-BRONZE ALLOYS.

By SERGIUS KERN, M.E., St. Petersburg.

LAST spring and summer we made experiments, which we are still continuing, on some nickel-bronze alloys; our aim was to produce castings from such alloys, to be used in mechanical work, especially for different fittings in high-pressure marine boilers.

The alloys rust very slightly, and in several cases are to be preferred to steel castings, more especially as the nickel-bronze castings made from our alloys No. I. and No. II. give very good results when mechanically tested.

Alloy No. I. corresponds to the English Admiralty's rules prescribed for ship-building steel, and alloy No. II. corresponds to the rules for steel castings (tensile strength 28 to 35 tons per square inch, with an elongation of 15 per cent in 2 inches).

Alloy No. I.

Copper	..	..	..	70.0 per cent.
Nickel	..	..	..	17.5 "
Zinc	..	..	..	12.5 "
100.0				

This alloy in the cast state gives a tensile strength of 26 tons, and 23 per cent of elongation, in 2 inches. Fracture, fibrous. Bending test, 67° over a radius of 1½ inch.

Alloy No. II.

Copper	..	..	..	70.0 per cent.
Nickel	..	..	..	20.0 "
Zinc	..	..	..	10.0 "
100.0				

This alloy gives excellent results: tensile strength 36 tons, with an elongation of 14 to 17 per cent, in a length of 2 inches. Fracture, also fibrous. Bending test, 35—40° over a radius of 1½ inch.

Drop Tests.

Weight of monkey, 18 kilogrms. Specimens from alloys Nos. I. and II., with a section of 30 m.m. square, gave a bend to a right angle, without fracture, after eleven consecutive drops of the monkey. The height of the fall of the monkey at the first drop was 1 metre and 1.5 metre at the eleventh drop.

We prepare our alloys Nos. I. and II. in the same manner, using ordinary copper crucible furnaces; each furnace contains one crucible, with a charge of 150 pounds. Half of the copper is melted beforehand with all the zinc; the alloy is poured into thin plates, ¾ of an inch thick, which are next sheared into small pieces.

For preparing the alloys we proceed as follows:—On the bottom of the crucible we place some nickel (in the form of cubes), next some copper-zinc alloy, and on the

latter some copper, going on in such a way till the crucible is filled up. On the top of the charge a layer of charcoal is placed. The melting of the 150 pounds charge takes about five hours.

The alloy is run into flat open moulds, and the slabs obtained are re-melted twice before being used for castings. At each melt about 0.75 per cent of zinc is added to the melted alloy, when the crucible is out of the furnace and ready to be poured into the mould.

The moulding is done exactly in the same way, concerning the sand, as when casting copper articles, but, as the alloys have a notable shrinkage in setting down, top ends must be placed on the castings, as is done with steel castings. After pouring the metal, the open top ends must be immediately covered with coarsely ground charcoal.

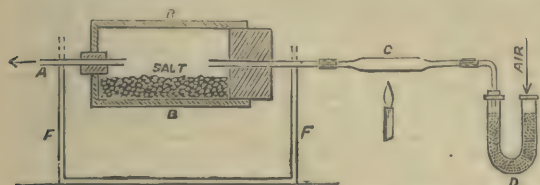
February, 1900.

A NEW DEVICE FOR DRYING CRYSTALLISED SALTS.

By F. H. GETMAN, F.C.S.

BEING at a loss for a clay tile some days since, when preparing some antimony sulphate, I was forced to devise some form of "dryer" from the materials at hand. My first apparatus was so satisfactory that I was led to improve upon it, and now I feel that it may be of service in other laboratories.

The apparatus is shown in the accompanying sketch, where B B represents a large-sized porous cup through the bottom of which is bored a central hole large enough to receive a good-sized single-hole cork. The mouth of the cup is also fitted with a cork through which passes a single hole, the axis of which passes through the hole in the bottom. These corks are fitted with glass tubing, as shown, and the whole placed in a frame, F F, which may be made from an ordinary box. The tube passing



through the large cork is connected either directly with the drying tube, D, or with D through the hard glass tube C. The tube A is connected with an aspirator. The salt to be dried is placed in B B, the corks inserted tight, the cup placed in its supports, connections made with the drying tube, and then the aspirator started at A.

From time to time the cup is slowly turned, thus exposing both a fresh surface of cup to the salt, and also a fresh surface of salt to the current of air. If it is desired to use warm air, the tube C may be inserted in the train and heated to any desired temperature. This arrangement will be found vastly superior to the clay tile, and, owing to the simplicity of construction, can easily be made in any laboratory however small.

Chemical Laboratory, Stamford High School,
Stamford, Conn., U.S.A.,
January 30, 1900.

Royal Institution.—On Thursday next (March 1st) at Three o'clock, Dr. Charles Waldstein, Slade Professor of Fine Arts, University of Cambridge, will deliver the first of a course of three Lectures at the Royal Institution, on "Recent Excavations at the Argive Horæum in Greece;" and on Saturday (March 3rd) Lord Rayleigh, Professor of Natural Philosophy, R.I., will begin a course of six Lectures on "Polarised Light."

NOTE ON THE DIRECT COMBUSTION OF METALLIC ALLOYS.

By HARRY BREARLEY.

THE estimation of carbon by igniting the metal in a stream of oxygen is said to have originated with Berzelius or Mulder. The difficulties of the process are practical ones; the finely-divided sample or the extremely high temperature required generally occasioning more trouble than a preliminary separation of the carbon. Where the sample is already in powder, however, or must be powdered for other operations, one objection to direct combustion no longer holds, and in such cases it seems worth while to enquire with what success the direct combustion may be resorted to when only easily available temperatures are used.

The term "direct combustion" is applied generally to the estimation of carbon in metals without previously separating it. There are processes of this kind, both wet and dry, in which a large variety of reagents are used; it is therefore necessary to say that here "direct combustion" refers to the simple ignition of the sample in a stream of oxygen without any reagent whatever.

Each of the following samples were passed through a sieve having 90 meshes to the linear inch, and, so as to indicate with what alloys the process is serviceable, the ignitions were limited to one hour, even when CO₂ was being slowly evolved at the end of that time. The furnace was of the ordinary Bunsen type, and the porcelain tube was supported in asbestos arches (CHEMICAL NEWS, lxxvii., 5). A temperature was thus obtained which made it impossible or very difficult to at once distinguish the boat on looking into the tube. This is hotter than combustion tubes generally are, but by no means hotter than can readily be attained with any other type of furnace, using the asbestos arches (obtainable from Becker, Hatton Wall, London, E.C.).

Material.	Direct ignition.	Actual C percentage.
Tungsten (metallic)	2.47	2.47
" "	0.65	0.64
" "	3.41	3.46
Ferro-tungsten (85 per cent)	5.75	5.64
" (50 ")	1.09	1.09
Ferro-silicon	2.04	2.00
"	1.59	1.55
12 per cent silicon-spiegel	2.31	2.35
12 "	2.30	2.26
20 " spiegel	6.01	6.11
20 "	4.94	5.02
Ferro-silico-molybdenum	1.58	1.56
Molybdenum (metallic)	4.69	4.72
70 per cent molybdenum-nickel	2.94	2.90
70 " tungsten-nickel	1.00	1.32
80 " ferro-manganese	2.82	7.01
60 " ferro-chromium	1.04	8.69
70 " chrome-nickel	1.53	6.65
Chromium (metallic)	0.44	5.13

Of those alloys set forth in the first part of the table, the 20 per cent spiegel is the only one of which there is any doubt of a perfect decarbonisation. The differences, however, are not such as invalidate the process for technical purposes, nor is the alloy one of those to which direct processes only are applicable.

The metallic molybdenum volatilises, leaving only such impurities as SiO₂, WO₃, &c.

The tungsten-nickel alloy has every appearance of being fully oxidised when drawn from the furnace, and repeated ignition yields no more CO₂; but ignition of the residue, or direct ignition of the sample with PbO₂ or Pb₃O₄ indicate a considerably higher percentage. It is noteworthy that ignition with either CuO or PbCrO₄ gives lower

figures than ignition with PbO_2 unless a very high temperature is used.

Ferro-manganese, ferro-chromium, chrome-nickel, and metallic chromium resist, with more or less completeness, all attempts to oxidise them without a reagent. Ferro-manganese, however, is not refractory in the sense that metallic chromium or ferro-chromium are. It is not plain why simple ignition decarbonises ferro-manganese so incompletely, unless it be that the hard-gritted surface protects the centre portions from oxidation. It is noteworthy that it decarbonises completely when mixed with such of the metallic oxides as have little or no effect on the chrome alloys. For example, 2 grms. intermixed with 2 grms. of ignited zinc oxide yielded—

6.98 instead of 7.01 per cent carbon
and 6.68 6.63 "

Metallic zinc had evidently been formed; there were tufts of crystalline ZnO on the edges of the boat.

Beyond greater simplicity, the advantages of combustion without reagents are:—As there is generally no fusion, the same boat is available time after time; there is no reagent blank to be ascertained, and allowed for; and, where strong reducing agents, like silicon and manganese, are present, no metallic beads (Cu or Pb), with the possibility of occluding some of the sample, can occur.

The choice of zinc oxide in particular cases rests on the facts that it is quite free from blank after ignition in the muffle, and any of the oxide reduced to metal is so readily re-oxidised that no metallic beads can vitiate the assay.

PREPARATION OF METALLIC TELLURIUM.*

By VICTOR LENHER.

EARLY in 1898 a study was begun on tellurium. The material at hand on which the research was to be made consisted of the so-called electrolytic copper slimes furnished by the Baltimore Electric Refining Company. The first step was naturally to extract the tellurium from these residues, then to work up the metal obtained into such derivatives as might be found convenient for study. The first method employed consisted in the treatment of the residues with concentrated hydrochloric acid; chlorides of the soluble elements were formed, while a highly siliceous residue remained insoluble. The resulting solution was poured into water, when the oxide of tellurium was precipitated along with more or less antimony oxychloride. This precipitate was again dissolved in hydrochloric acid and sulphur dioxide conducted into the solution, when tellurium was precipitated in a finely divided condition.

A process similar to the above is at present the general way by which the metal is obtained. The German tellurium which is on the market is obtained by treatment of the ore with aqua regia and the subsequent precipitation from a hydrochloric acid solution by sulphur dioxide.

A number of methods for obtaining metal are known, but most depend on the precipitation of the tellurium from a hydrochloric acid solution by sulphur dioxide.

Berzelius fused the naturally recurring tellurides with a mixture of oil and soda or potash, or with potassium tartrate. He obtained purple potassium telluride, which, subjected to the moderate oxidation of a current of air, yielded tellurium according to the equation $\text{K}_2\text{Te} + \text{O} + \text{H}_2\text{O} = 2\text{KOH} + \text{Te}$.

Berthier treats nagyagite, which is a combination of gold telluride and lead sulphide, with hydrochloric acid; hydrogen sulphide is evolved, lead, antimony, &c., pass into solution, while the gold telluride is unattacked. The latter is treated with nitric acid, which dissolves the tel-

lurium away from the gold. The tellurium is brought into hydrochloric acid solution by evaporation with hydrochloric acid, and the tellurium precipitated by sulphur dioxide. Petzite is fused with a mixture of sodium carbonate and potassium nitrate. He extracts the tellurate with water, treats with hydrochloric acid to reduce to tellurite, after which he precipitates with iron. Berzelius extracts in a similar manner, but reduces his tellurate to telluride by fusion with carbon.

Schroetter treats tellurides with either hot concentrated sulphuric acid or aqua regia. The gold is precipitated with ferrous sulphate or oxalic acid and the tellurium by zinc. He re-precipitates the tellurium from a hydrochloric acid solution by sulphur dioxide or an alkaline sulphite. Another method of extraction is to treat the ore with chlorine gas, when tellurium chloride is formed and distils from the non-volatile portion. The tellurium is subsequently precipitated from hydrochloric acid solution by sulphur dioxide. The method doubtless owes its origin to Berzelius. It has also been suggested to prepare tellurium by precipitation with the electric current.

In 1870 Stolba called attention to the precipitation of tellurium from its alkaline solutions by means of grape-sugar; later, Kastner found that it was completely precipitated by grape or invert sugar. But after those two papers the sugar precipitation has been very little heard of; it seemed as though it should be an ideal means of producing metal from the electrolytic copper residues, as the tellurium appears as a waste product and is already in alkaline solution.

A series of experiments was made to attempt the extraction of tellurium by different methods. The first thing to do was to prepare tellurium by a well-known method and obtain a product that it would be possible to use in comparison. To this end, 5 pounds of residues were treated with concentrated hydrochloric acid (sp. gr. 1.20). An amber-yellow liquid was obtained, and a residue which was highly siliceous. It is possible to obtain a perfectly clear solution by filtration through asbestos wool, using a suction-pump. When sulphur dioxide is brought into contact with such a strong acid solution, selenium should be precipitated free from tellurium according to Keller (*Journ. Amer. Chem. Soc.*, xix., 773). When sulphur dioxide was introduced into this solution a red precipitate formed, showing selenium was just precipitated. It appeared to darken, however, when the liquid was saturated. On boiling, the precipitate agglomerated into a mass which much resembled selenium, but, on separating it by means of potassium cyanide, it was found to consist of 3.2 grms. of selenium and 28.3 grms. of tellurium. This seems to indicate that tellurium and selenium cannot be perfectly separated by sulphur dioxide in strong hydrochloric acid solution. The filtrate from the strongly acid solution was diluted with water, and more sulphur dioxide passed through the liquid, when the rest of the tellurium was precipitated. The lump of metal which was formed by fusion was finely powdered and fused with potassium cyanide; purple telluride of potassium was formed. The solution was filtered and a current of air passed through. The tellurium which was formed was fused, then distilled in hydrogen gas. This material was considered pure. When treated with aqua regia, dioxide is formed and may be obtained by evaporation. Tellurium oxide is completely volatile at a low temperature in hydrochloric acid gas, no residue remaining. Pure tellurium is likewise completely volatile when heated in hydrogen.

Since it seems most natural to prepare a metal from its oxide, the tellurium oxide was subjected to a number of reduction tests. In recent years, metallic magnesium and metallic aluminum have shown themselves to be of great value as reducing agents. When metallic aluminum and tellurium oxide are heated together in a crucible a violent reaction takes place, tellurium is formed, but immediately unites with the aluminum, forming aluminum telluride. Metallic magnesium, even in very coarse condition, when heated with tellurium oxide, gives a very explosive reaction.

Contribution from the Havemeyer Laboratories of Columbia University. From *The Journal of the American Chemical Society*, Vol. xxi., No. 4.

So very energetic is the action that it has not been possible to collect any of the products formed.

When dry glucose is heated with the oxide, a coke is formed which becomes coated with the metal and is difficult to fuse into a button. The same may be said of a dry fusion of asphaltum with the oxide. Ignition of the oxide with dry oxalic acid does, however, give metal readily, and fusion into a globule is an easy matter.

The next series of experiments was made with the sugars. Tellurium oxide was dissolved in potassium hydrate, cane-sugar was added, and the solution warmed. When a saturated solution is used, purple telluride is formed, but boiling in contact with the air causes a rapid separation of black tellurium. After washing with water the precipitate can be dried and fused into a mass.

From a solution of an alkaline tellurite, glucose precipitates black elementary tellurium. No intermediate formation of telluride could be noticed as with cane-sugar. Pure white anhydrous grape-sugar was dissolved in water and added to a warm solution of the alkaline tellurite. Tellurium was precipitated in elementary form. During the process of washing, which always followed the precipitation, it was invariably noticed that grape-sugar was much more difficult to remove from the finely divided tellurium than any of the other sugars.

From these experiments it seemed natural to conclude that reducing sugars will give a very practical method for the preparation of metallic tellurium. Tellurium obtained by this method is completely volatile in hydrogen gas, and its oxide is likewise volatile in hydrochloric acid gas.

Thanks to the kindness of Mr. Walker, of the Baltimore Electric Refining Company, who furnished the residues, and to Prof. P. de P. Ricketts, who in so many ways made the work possible, the author has been enabled to prepare a bar* of tellurium by fusion of the finely divided material obtained by reduction of tellurium in alkaline solution by means of sugar.

Among other experiments, I decided last year, while working on selenium, that as soon as I could obtain satisfactory compounds I should determine the atomic mass of tellurium by precipitation with hydroxylamine. As my work thus far on tellurium, which was begun with Prof. E. F. Smith at the University of Pennsylvania, and is now going on in this Institution, had for one of its objects the determination of the atomic mass of tellurium by means of the hydroxylamine precipitation, it seems quite proper that I should continue it, notwithstanding the fact that Prof. Jannasch, of the University of Heidelberg, announced in the *Berichte* for October, 1898, that he is engaged in work on the same line.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 1st, 1899.

Professor THORPE, F.R.S., President, in the Chair.

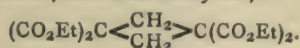
(Concluded from p. 82).

14. "On the Condensation of Formaldehyde with Ethyl Malonate and on the Synthesis of Pentamethylenetricarboxylic Acid." By J. FRANK BOTTOMLEY and W. H. PERKIN, jun.

In a previous communication by Haworth and Perkin (*Trans.*, 1898, lxxiii., 330), it was shown that the following substances are formed, either directly or indirectly, by the condensation of formaldehyde with ethyl malonate.

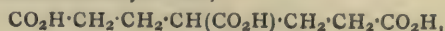
1. Ethyl methylenemalonate, $\text{CH}_2\text{:C}(\text{CO}_2\text{Et})_2$, and two polymerides called respectively ethyl *para*-methylenemalonate and ethyl *meta*-methylenemalonate. 2. Ethyl

propanetetracarboxylate, $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$. 3. Ethyl tetramethylenetetracarboxylate,—



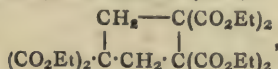
In the present paper, the authors show that, under certain conditions, ethyl pentanehexacarboxylate, $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, is formed by the condensation of 3 mols. of ethyl malonate with 2 mols. of formaldehyde. This new ester is crystalline, melts at 53–55°, and, when digested with baryta, is decomposed with formation of an acid which is evidently propanetetracarboxylic acid, $(\text{CO}_2\text{H})_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$, since on heating at 240° it yields glutaric acid.

Pentanetricarboxylic acid,—

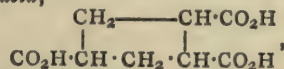


is formed when ethyl hexacarboxylate is hydrolysed with dilute hydrochloric acid, and the resulting acid heated at 200°; it melts at 113–114°, and has already been described by Emery (*Ber.*, 1891, xxiv., 284). When ethyl pentanehexacarboxylate is heated with sodium ethylate and methylene iodide, it yields ethyl paramethylenemalonate—a remarkable decomposition, which is discussed in the paper.

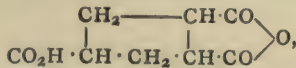
Ethyl pentamethylenehexacarboxylate,—



is formed when the disodium compound of ethyl pentanehexacarboxylate is treated with bromine, and when hydrolysed yields pentamethylene hexacarboxylic acid (m. p. 212°). By the elimination of carbon dioxide from this acid, the *cis*- and *trans*-modifications of pentamethylenetricarboxylic acid,—



have been prepared; the former melting at 146–148°, the latter at 127–130°. Anhydro-*cis* pentamethylenetricarboxylic acid,—



obtained by heating the *cis*-acid with acetic anhydride, melts at 215–217°, and when treated with water it is again converted into the *cis*-acid.

Experiments are also described on the distillation of the *para*- and *meta*-polymerides of ethyl methylenemalonate, and on the hydrolysis of these polymerides and of ethyl methylenemalonate itself.

15. "The Volumetric Estimation of Potassium." By R. H. ADIE, M.A., and T. B. WOOD, M.A.

The method proposed by the authors is to precipitate the potassium as cobaltinitrite (of which the formula is usually given as $\text{K}_6\text{Co}_2(\text{NO}_2)_{12}\cdot 3\text{H}_2\text{O}$) and to titrate the nitrite with a standard solution of potassium permanganate in acid solution. The experiments of the authors so far seem to show that there are three, instead of two, nitrite groups for each atom of potassium, and that the precipitate they obtain is probably an acid salt, as the ratio of the cobalt to the nitrite is that indicated by the above formula.

The method is as follows:—The solution containing the potassium to be estimated is freed from other bases as far as possible, by means of sodium carbonate, then concentrated if the solution is at all weak, acidified with acetic acid, and excess of a solution of sodium cobaltinitrite added. The mixture is allowed to stand for twenty-four hours, the precipitate collected on a Gooch filter, washed several times with 10 per cent acetic acid, and finally once with water. The asbestos filter and the precipitate are now transferred to a beaker and boiled with a dilute solution of soda, filtered, and made up to 100 c.c.

* This bar was exhibited before the American Chemical Society at New York, and weighed four pounds.

Of this solution 20 c.c. are taken, acidified with dilute sulphuric acid, and rapidly titrated with the permanganate solution. A second fraction of 20 c.c. is taken, and to this the amount just found of permanganate solution is added, then acidified, and the end-point again determined. In one estimation, the volumes required were 16.3 and 16.4 respectively. The end of the reaction is more easily obtained if the permanganate is added to the nitrite solution in excess and the excess determined by potassium iodide and thiosulphate solution.

On testing the method with pure potassium salts, it was found that the results, whilst very concordant amongst themselves, gave results too high in almost exactly the proportion 3 : 2; 1 c.c. of the permanganate solution used was in this way found to correspond only to 0.0077 grm. of K_2O instead of to 0.01175, the value calculated from the formula given above. This seems to indicate for the precipitated salt some formula such as $K_2HCu(NO_2)_6$.

As examples of the accuracy of the method the following analyses are given:—

I. Kainite—

	I.	II.	Mean.
K_2O per cent ..	12.22	11.94	12.13
By platinochloride method—			
K_2O per cent ..	11.98	12.07	12.03

II. Commercial potassium sulphate—

K_2O per cent ..	50.05	50.82	50.44
By platinochloride method—			
K_2O per cent ..			50.80

III. Soil—

	I.	II.	III.	IV.	Mean.
K_2O per cent	1.09	1.20	1.06	1.05	1.10
By platinochloride method—					
	1.11	1.25	0.98	0.97	1.08

The authors are engaged in making a more complete investigation of the composition of the precipitated cobaltinitrite and its decomposition by alkalis, as well as the application of the method to the determination of cobalt.

16. "On the Action of Aluminium Chloride on Camphoric Anhydride." III. By F. H. LEES and W. H. PERKIN, jun.

The authors have already published two notices of their work on the action of aluminium chloride on camphoric anhydride (*Proc.*, 1898, xiv., 111; and 1899, xv., 23), and in spite of this, M. Blanc (*C. R.*, 1899, cxxix., 1019; *Chem. Centr.*, 1900, i., 199) has lately undertaken an investigation of the new substances formed in this reaction which were first obtained by the authors, the examination of which was expressly reserved by them. The authors are therefore compelled to publish the results they have obtained, although the investigation is still incomplete.

When camphoric anhydride reacts with aluminium chloride at ordinary temperatures, the principal product is *isolaunonic acid*, $C_9H_{14}O_2$, but there is also formed a lactone, $C_9H_{14}O_2$, called by the authors *ψ-campholactone*. This lactone, on hydrolysis with alkalis, yields two hydroxy-acids, $C_9H_{16}O_3$, which melt at 113° and 161° respectively (the melting-points 109° and 152° previously given are too low).

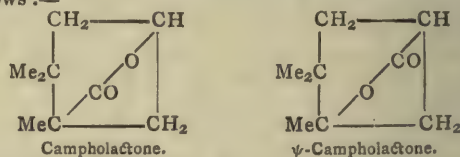
When dissolved in a solution of hydrogen bromide in glacial acetic acid, *ψ-campholactone* is converted into a mixture of bromo-acids, $C_9H_{15}BrO_2$. One of these is liquid, but the other is a solid melting at 128–130° with decomposition, which when boiled with glacial acetic acid loses hydrogen bromide with formation of an unsaturated acid, $C_9H_{14}O_2$ (m. p. 73°).

Attempts to reduce the solid bromo-acid with zinc dust and acetic acid led to the formation of a new lactone, $C_9H_{14}O_2$, which melts at 44°, and when hydrolysed with baryta water is converted into the same hydroxy acid,

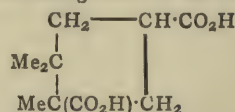
$C_9H_{16}O_3$ (m. p. 113°), which is obtained by the hydrolysis of *ψ-campholactone*.

Probably *ψ-campholactone* and this new lactone are stereoisomeric, and the same remark applies to the two hydroxy-acids melting at 113° and 161°.

It was stated in one of the previous communications (*Proc.*, 1899, xv., 23) that, when *ψ-campholactone* is treated with phosphorus pentabromide and the product poured into methyl alcohol, *methyl bromo-dihydro-ψ-launonolate* is obtained, and that this methyl ester, on hydrolysis, yields an oily unsaturated acid, $C_9H_{14}O_2$, called *ψ-launonic acid*. Since the publication of these results, it has been found that this oily acid, on standing for some weeks, deposits crystals which melt at about 69°, and it is evident that the oily acid is a mixture of two isomeric acids, $C_9H_{14}O_2$, which again are probably stereoisomeric. It was also suggested (*Proc.*, 1899, xv., 24) that campholactone and *ψ-campholactone* are possibly closely related, and that this relationship might be represented as follows:—

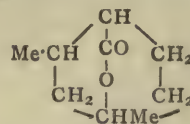


These expressions being based on the formula—



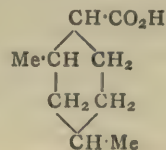
which is one of those suggested by Perkin as possibly representing the constitution of camphoric acid.

When, however, it is remembered that *ψ-campholactone* dissolved in concentrated sulphuric acid, is almost quantitatively converted into xylic acid at 90°, and that, as has since been found, *ψ-launonic acid* yields the same acid on prolonged treatment with sulphuric acid at ordinary temperatures, it seems possible that *ψ-campholactone* may after all be the lactone of *hydroxyhexahydroxylic acid*,—



It will be very difficult to prove whether *ψ-campholactone* is a 5 or 6 ring derivative, since experiments which were made on a considerable scale, with the object of reducing *ψ-launonic acid*—in which case either dihydroisolaunonic acid or hexahydroxylic acid should have resulted and could have been identified—failed owing to the fact that *ψ-launonic acid* is not appreciably attacked even by repeated and prolonged treatment with amyl alcohol and sodium.

When a chloroform solution of camphoric anhydride is left for some weeks in contact with aluminium chloride, the *ψ-campholactone* remains unchanged, but the *isolaunonic acid* almost entirely disappears, and in its place two saturated acids, $C_9H_{16}O_2$, are found; these have now been separated partly by freezing and partly by means of their crystalline amides. One of these acids is solid, melts at 77°, and is identical with the *hexahydroxylic acid*,—



which Bentley and Perkin (*Trans.*, 1897, lxxi., 173) obtained by the reduction of xylic acid. The other acid, $C_9H_{16}O_2$, is an oil and it is probable that this and the solid acid represent the *cis*- and *trans*-modifications of hexahydroxylic acid. When the acid melting at 77° is treated with bromine and subsequently with alcoholic potash, it yields a solid acid, $C_9H_{14}O_2$ (m. p. 107°), which is identical with the tetrahydroxylic acid prepared by Bentley and Perkin (*loc. cit.*).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 5, January 29, 1900.

Study of the Rays of Radium.—H. Becquerel.—The portions of the radium rays which are deviated by the magnetic field lend themselves to various experiments, from the study of which the author has found—(1). The influence exerted by air on the velocity of propagation of the rays in question, by making measurements in a vacuum. However, he observed no appreciable difference between vacuum and air measurement. (2). The identification of rays emitted by variously active radiferous salts. (3). The form of the trajectory of the rays in a uniform magnetic field. (4). The dispersion in the magnetic field. (5). The existence of electrostatic charges in the presence of very minute material masses.

Molecular Volumes of some Camphor Derivatives.—A. Haller and P. Th. Muller.—The authors' experiments show that the decrease of volume corresponding to the actual addition of the two radicals to form camphor is about 23 c.c. per litre, and is less for toluenic solutions, which are nearly a quarter normal. This number, which is still considered provisional, allows nevertheless of fixing in a sufficiently accurate degree the molecular weight of camphor compounds by the method of densities. It allows also the disclosure of the existence and production of new closed chains in the derived molecule of camphor.

Retention of Silver Chloride by Mercurous Chloroamide.—F. Leteur.—To estimate silver in presence of mercury, the usual plan is to treat the mixture of the two chlorides with aqueous ammonia. The mercurous chlorides is transformed into mercurous chloroamide, NH_2Hg_2Cl , and the silver chloride is dissolved. This simple method succeeds when the latter substance exists in a tolerable quantity in the mixture, but it is insufficient when the contrary is the case, the complex mercurous compound retaining always some silver chloride. The author having examined the nature and quantity of this retention suggests the following method of procedure:—The residue from the treatment of the mixed chlorides with aqueous ammonia is digested in the cold with concentrated nitric acid, to which is added sufficient hydrochloric acid to transform the chloride of mercurous-ammonium into mercuric chloride. In the case of the presence of silver, there remains a white residue, which is not blackened by aqueous ammonia and is totally soluble in this reagent. If the residue does not present this character another treatment must be performed.

Action of Copper on Acetylene. Formation of a Highly Condensed Hydrocarbon—Cuprene.—Paul Sabatier and J. B. Senderens.—The author's experiments on the action of a mixture of excess of hydrogen and acetylene on various metals shows that iron and cobalt behave in the same manner as nickel; the action of the latter having been discussed in a former paper. Copper, however, appears to exert a special reaction on acetylene alone. The resulting product is a yellow solid, which is

apparently built up of a mass of very fine filaments. It burns quickly, giving out an aromatic odour, and leaving a slight black residue of cupric oxide. It is evidently a hydrogen carbide. Analysis shows that the relation between the carbon and hydrogen is 14:1. On account of its method of formation the name cuprene is proposed, the formula being C_7H_6 . When heated to above 400° it decomposes, evolving complex products, and leaving a solid residue of carbon.

Acidimetry of Polybasic Organic Acids.—A. Astruc.—This paper contains an account of further experiments on the action of polybasic organic acids on various indicators, and is a continuation of the author's work with M. Henri Imbert, which was published in a previous paper.

Isopyromucic Acid.—L. T. Simon.—Pyromucic acid was discovered as one of the products of distillation of mucic acid, being produced according to the equation, $C_6H_{10}O_8 = C_5H_4O_3 + CO_2 + 3H_2O$. In 1873 Limpricht, whilst repeating this distillation, isolated as a by-product an acid which he considered as an isomer of the preceding acid. The author repeats this experiment and succeeds in preparing the latter acid exclusively. The isopyromucic acid thus prepared is white when pure, very soluble in alcohol, ether, and water, and but slightly soluble in carbon disulphide.

NOTES AND QUERIES.

*.† Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Water Analyses.—(Reply to N. H.).—The quantity of $CaSO_4$ present is excessive, and would in itself be sufficient to render the water undesirable for drinking or domestic purposes; 30 parts of total hardness and 50 parts of total solids per 100,000 is the maximum that a potable water should contain.—W. A. JENKIN, Rio Tinto Laboratory, Spain.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.

Society of Arts, 4.30. "Agricultural Education in Greater Britain," by R. Hedger Wallace.

WEDNESDAY, 28th.—Society of Arts, 8. "Pneumatic Dispatch," by Prof. Charles A. Carus Wilson, M.A.

THURSDAY, March 1st.—Royal Institution, 3. "Recent Excavations at the Argive Heraeum (in Greece)," by Charles Waldstein, Litt D., Ph.D., L.H.D. Chemical, 8. "Pilocarpine and the Alkaloids of Jaborandi Leaves," by H. A. D. Jowett, D.Sc. "Isomeric partially Racemic Salts containing Pentavalent Nitrogen" (Parts I.—VII.), by F. S. Kipping, D.Sc., F.R.S. "New Synthesis of Indene," by F. S. Kipping, D.Sc., F.R.S., and H. Hall. "Potassium Nitrito-hydroximidisulphates and the Non-existence of Dihydroxylamine Derivatives" and "Identification and Constitution of Fremy's Sulphazotised Salts of Potassium," by E. Divers, D.Sc., F.R.S., and T. Haga, D.Sc. "Some Acids obtained from α -Dibromocamphor," by A. Lapworth and E. M. Chapman.

FRIDAY, 2nd.—Royal Institution, 9. "Malaria and Mosquitoes," by Major Ronald Ross, D.P.H., M.R.C.S.

Physical. (Special Meeting in the Physical Laboratory of University College. The Laboratory will be open and tea served at 4.30). "The Relative Rates of Effusion of Argon, Helium, and some other Gases," by Dr. F. G. Donnan. "On the Distillation of Liquid Air and the Composition of the Gaseous and Liquid Phases," by E. C. C. Baly. "The Reversibility of Galvanic Cells," by T. S. Moore. "On the Damping of Galvanometer Needles," by M. Solomon.

SATURDAY, 3rd.—Royal Institution, 3. "Polarised Light," by The Rt. Hon. Lord Rayleigh, M.A., D.C.L. &c.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2101.

NOTE ON THE DETERMINATION OF NITRIC NITROGEN BY SCHLÖSING'S METHOD.

By C. DAVIDSON.

THE distinctive feature of de Koninck's apparatus (*Zeit. Anal. Chem.*, xxxiii., 200), abstracted in *Journal of Chemical Society*, 1894, ii., 296) is the capillary delivery tube which dips under mercury, and is longer than a barometer-tube, so that the functions of the troublesome stopcocks or slips, usual in apparatus for this purpose, are automatically performed. The following slight modification of de Koninck's apparatus, besides practically eliminating the error due to the solubility of nitric oxide in water, has proved very convenient in actual use during the last two years.

The principle of the apparatus is to substitute for de Koninck's mercury trough and large cylinder of water a modified Schiff's nitrometer, which is rather more convenient to handle, although initially more troublesome to make.

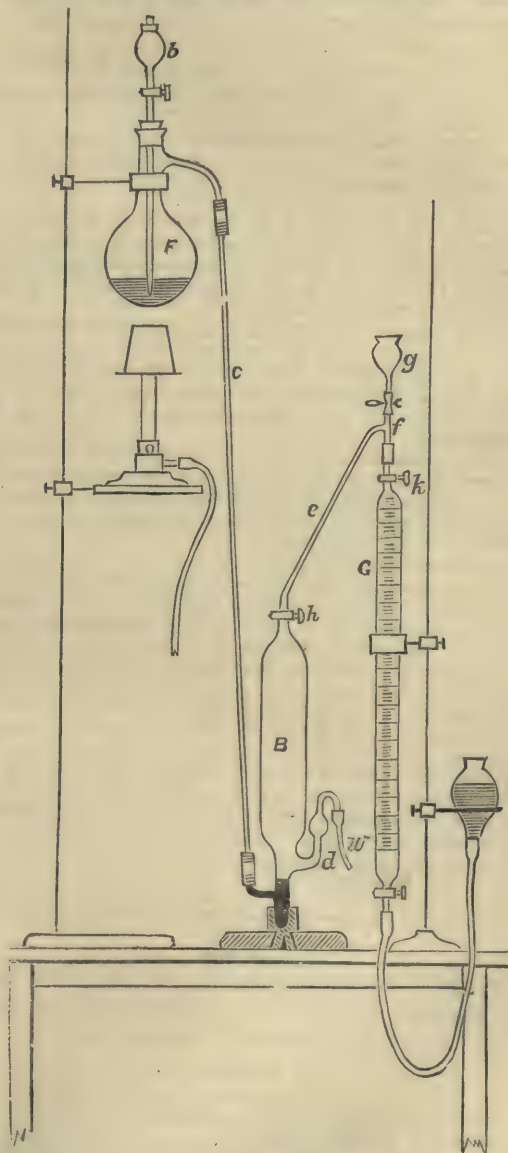
Apparatus.—The stoppered funnel *b* has a capacity of about 50 c.c., and should if possible have a capillary stem. *F* is a distilling flask of 250 c.c. capacity, with its side-tube bent almost perpendicularly. The tube *c* is of fine bore—in my own apparatus about 0.2 c.m. diameter—and of such length that the difference of level of its two ends is about 80 c.m. Joints of thick-walled rubber tubing have proved quite safe if well corded. The tube *B* is really a modified Schiff's nitrometer; the capacity of the wider part is about 200 c.c.; the narrower part at the bottom is about 1.5 c.m. in bore and 6 c.m. long between the two side-tubes. The tube *d* is blown on so that its upper-side slopes continually upwards towards *B*, while its underside is at least level. The tubes *e* and *f*, forming a *T* which connects *B* on the one hand to a gas-burette (capacity 100 c.c.), and on the other to a small bulb, *g* (whose use is obvious), are both capillary. The lower part of *B* is filled to within a c.m. of *d* with mercury. The rubber tube *w* communicates with a tubulated bottle, *w* (not shown in the sketch), containing air-free water.

Procedure.—Forty c.c. of a solution of FeCl_2 , containing 20 per cent Fe (made from wrought-iron nails and HClAq , air being excluded by a layer of light petroleum), together with an equal bulk of HClAq of sp. gr. 1.10, are placed in the flask *F*. The stem of the funnel *h* is filled with water; and the reservoir *w* having been filled with (warm) water from which the air has been expelled by boiling, the tube *B* and the capillary *e* are filled with water therefrom. The burette *G* should not be connected up as yet.

Heat is applied to *F* by means of a small Bunsen-flame whose tip just touches the flask; and the heating is continued until all the air has been boiled out into *B*, whence it is removed, from time to time if necessary, through *e*, *f*, by keeping *w* high and opening the stopcock of *B*. When air ceases to come over, the Bunsen is removed (or lowered on its rest until the mercury in *c* is just kept stationary), *B* is completely filled with water from *w*, the overflow going out through *f*; the gas-burette, *G*, charged with air-free 7 per cent NaOHAq , is joined on at *f*; any air-bells remaining in *f* are removed by raising the burette-reservoir and opening the stopcock and clip. Enough soda solution should be allowed to flow through to half-fill the bulb *g*; it will be useful afterwards.

Such a quantity of the solution of the substance to be operated on as corresponds to about 0.2 grm. of NaNO_3 is

placed in the funnel *h*, and carefully run into *F*. The funnel is rinsed out three times with 10 c.c. of HClAq , of sp. gr. 1.10, care being taken, of course, to keep out air; *w* is placed high and the burette-reservoir low, and heat is cautiously applied to *F*. If the mercury in *c* is at this point more than half-way up, the heating must be very gentle at first (a Bunsen-flame an inch long, and sheltered by a funnel, should be placed with its tip about 2 inches below the flask, to begin with), but as the mercury falls the heat may be increased, until when the liquid is boiling



under atmospheric pressure no special care is necessary. By simply opening the two stopcocks, *h* and *k*, the NO is transferred from time to time to the gas-burette (the lower stopcock of which is of course open all this time).

When all the NO has been boiled out of *F*, it is swept into the burette finally by raising *w* sufficiently and opening *h* and *k*; if any small bubble sticks at the join of the *T*, it is removed by closing *h*, keeping *h* open, and opening the clip of *g*, which was half-filled with soda-solution at the start. When the bubble has gone into

the burette, & is closed and then the clip; the burette is removed, cooled suitably, and the volume of the gas noted, together with the temperature and barometric height at the time. During the cooling it is well to close the lower stopcock of the burette, and invert the latter once or twice, in order to keep fresh soda in contact with the gas.

"Bunsen's 'Gasometrische Methoden' (second edition) contains a table giving the tensions of vapour of water given off by such a caustic soda. If this table is not at hand, subtract from the tension of pure water the following correction:—

At 10° to 15° C.	1·1 m.m.	} Kreusler.
At 15° to 25° C.	1·4 m.m.	

And the result is right to within $\pm 0\cdot2$ m.m. of mercury."—Dittmar, "Quantitative Analysis," p. 89.

One need not be painfully exact about this correction of the vapour tension, for the error caused by neglecting to make the above subtraction is in the worst case stated less than $+0\cdot16$ c.c. per hundred of NO.

As to the error caused by the solubility of the gas in water, it was found that the substitution of a reservoir of boiling water (kept boiling during the experiment) for W had no effect on the result. The error in question must therefore be very small.

A determination, including the preliminary boiling-out of the air, can easily be performed within an hour; and (as the FeCl_2 used suffices for over 800 c.c. of NO) if a number of determinations be performed consecutively, the average time of a determination is not much over half-an-hour.

The apparatus may very conveniently be mounted on a low stool, about 18 inches high, having a retort-rod 3 feet long screwed into it, and preferably provided with casters on two of its legs, so that it may be wheeled into a corner when no longer required.

In concluding, the author thinks it not out of place to utter a word of warning with regard to the practice, prevalent in some quarters, of attempting to compensate for inexact methods of analysis by comparing the results of two "parallel" experiments—one on an unknown substance, and the other on a standard whose content of the constituent sought is assumed to be known. Such methods are at best of but limited application. In many cases the purity of the standard may be doubted, while in others the precautions necessary to ensure that the parallel experiments are really being worked under exactly similar conditions are as laborious as those which would have to be taken in order to eliminate the errors whose effects are sought to be compensated.

37, Herriet Street, Pollokshields,
Glasgow.

ON THE DEGREE OF PULVERISATION OF THE RAW MATERIALS IN THE MANUFACTURE OF CARBIDE OF CALCIUM.

By B. CARLSON.

THERE is still a good deal of difference of opinion as to the degree of pulverisation necessary for the raw materials in the manufacture of carbide of calcium. If we obtain the same returns with a mixture of finely powdered lime and coke as with a coarsely powdered one, the second is evidently to be preferred from the economic point of view.

Now the heat necessary for the reaction may be divided into the heat of the reaction proper, and the heat necessary to bring the raw materials to the necessary temperature. Neither the specific heat, nor the heat of fusion of solid bodies, depends on their degree of fineness; it is the same for the heat of combination which is determined when the temperature is reached. A finely powdered material and an intimate mixture would only be necessary

if:—1. It was difficult to reach the temperature of the formation of carbide in the electric furnace; 2. If neither one nor the other of the raw materials, coke and lime, were liquid at the temperature obtained in the furnace; and 3. If no liquefied body was produced in which the raw materials could dissolve. In such a case, it would be necessary to bring into the zone of formation of the carbide as intimate a mixture as possible. Now, neither one nor the other of these conditions are fulfilled in this industry. The temperature at which the carbide is produced is decidedly lower than that of the electric furnace, and the lime also melts well below this temperature. The product of the reaction is, further, a solvent of lime and of carbon.

The process of the formation of carbide of calcium should be the following:—The lime should melt first and the coke dissolve in it, with the production of carbide of calcium. This reaction is absolutely analogous to that which takes place between iron and dilute sulphuric acid, for example. A solid body dissolves in a liquid with the evolution of gas. Under these circumstances the degree of subdivision of the material is absolutely unimportant.

So much for the theoretical point of view; we will now show that it is confirmed by practice.

If the mixture of lime and coke is in the state of powder, the carbonic oxide gas is unable to escape freely, and an empty space is formed round the igneous zone; the sides of this space are quickly brought to a high temperature by the radiation from the arc, and a species of lining of carbide is produced,—that is to say, a short circuit is formed between the electrodes. The pellicle thus formed has a certain resistance, and it is only after the lapse of a certain time that it suddenly explodes under the pressure of the carbonic oxide continually being formed. The gases make a passage through the charge, carrying with them a considerable quantity of fine powder; other explosions, arising from the mixture of carbonic oxide and air, and resulting from the furnace not being air-tight, are easy to prevent. The passages formed by the gases last for a certain time; their sides, formed of slightly conducting materials, rapidly take the temperature of the carbonic oxide, and this latter escapes from the furnace at approximately the temperature of the arc. It has been said that the temperature of the carbonic oxide ought to be considerably lower, since, being a product of solid coke and lime, it should absorb the heat in becoming gaseous. This would be true if, as soon as it was formed, the gas was removed from the action of the arc; but as this is in no way the case, it rapidly acquires a temperature near that of the arc. As soon as the passages of which we have spoken become obstructed, the production of a bulb of gas, and the other phenomena described, recommence.

Each time this takes place, a certain quantity of the comparatively cold substance falls into the zone of action of the arc, and causes the resistance to vary. It is for this reason that such large variations of current are met with in most manufactories of carbide. The dynamos also suffer from these variations after a time, and they should be prevented as much as possible. It is of course true that the bad effects can be avoided by having more powerful generators, but that leads to a larger capital outlay on the factory.

In certain factories the bubbles of gas are broken by wooden sticks as soon as they form; but even this remedy is insufficient, and necessitates very exhausting work.

These disadvantages can be entirely removed by substituting, for the powdered mixture, pieces the size of a nut. The gases produced pass freely throughout the mass, which they warm up, and escape from the furnace at a maximum temperature of 1000—1100°: as the temperature of the arc is generally 3000—4000°, the difference represents a considerable quantity of heat given to the raw materials; these latter are further, in this case, completely deprived of water and carbonic acid, and the removal of these impurities increases the return to some

extent. The current passing through the furnace also becomes more constant.

By using a coarsely powdered material we can prevent both the production of dust and the inconveniences which accompany it. The gases traverse the layer of material not yet brought into action, and thus the expense of special apparatus to effect this is avoided.

When the mixture of lime and carbon is finely powdered, the gases carry off much more carbon, which is light, than lime, and an excess of this more expensive material has therefore to be used; further, we can never be sure what the proportions of the mixture are. When the manufacture is interrupted, the residue remaining in the furnace cannot be made use of without a preliminary analysis. This drawback has been remedied by making the residual dust into bricks, but it is more simple only to use the raw materials coarsely broken up. The loss of carbon is then reduced to a minimum, and it is not necessary to use more than the theoretical quantity. The equation $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$ shows that 1440 kilos. of raw material are required to obtain 1 ton of carbide. At the "Deutsche Gold-und-Silber-Scheide Anstalt," at Frankfurt-on-Maine, 1590 kilos. were used, while at some factories, where the powder was used, as much as 3000 kilos. were required. With coarsely powdered material it is only necessary to take a few precautions, very simple but indispensable for the success of the operation; it may be for this reason that it is so seldom used.

M. Pfleger, in 1897, made some conclusive experiments on this subject. Intermittent manufacture is more advantageous than continuous working, and all inconvenience due to dust in the furnace is got rid of.—*Zeitschrift für Elektrochemie*, vi., p. 325.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
 and
 PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 12th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during January was 2.30 inches, very evenly distributed throughout the month; the average fall is 2.16 inches. This makes an excess of 0.14 inch, or 6.4 per cent on the thirty years' average.

Our bacteriological examinations of 557 samples have given the results recorded in the following table; we have also examined 36 other samples, from special standpipes, &c., making a total of 593 samples:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	621
New River, filtered (mean of 131 samples) ..	10
Thames, unfiltered (mean of 27 samples) ..	2235
Thames-derived water, from the clear-water wells of eight Thames-derived samples (mean of 306 samples) ..	22
Ditto ditto highest	292
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	694
River Lea, from the East London Company's clear-water well (mean of 41 samples) ..	7

These results show that during the past month the London water supply has been highly satisfactory, both bacteriologically and chemically.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
 JAMES DEWAR.

ON THE MODIFICATIONS OF KJELDAHL'S METHOD FOR THE ESTIMATION OF NITROGEN.

By A. ATTERBERG.

K. WEDEMEYER has shown that the estimation of nitrogen by Kjeldahl's method can be effected in an hour; this statement caused me to make the following experiments:—

I first of all compared the various modifications of Kjeldahl's method, as they are described in König's book ("Unters. d. Landw. Stoffe," 2nd edition, p. 133), and specially noted the length of time required by the different oxidising agents to obtain complete oxidation and decolouration of the liquid. The material to be oxidised was represented by an earth containing 15 per cent of water and leaving 7 per cent of ash. The following are the results obtained:—

Method No. 1, with the addition of mercury ..	Minutes.
" " 2, " " ..	45
" " 3, " " ..	about 55
" " 4, " " ..	55
" " 5, " " ..	55
" " 6, without, " " ..	95
" " 7, " " ..	95

The acceleration of the oxidation by the addition of mercury caused me to pursue my investigations in the same direction, and my experiments were carried out on the same sample of earth. I may also mention that all my experiments were carried out in flasks of 250 c.c. capacity, except where the contrary is stated.

	Minutes.	
Gunning's mixture (20 c.c.) without mercury	95	With abundant froth.
The same, with 1 drop of mercury ..	55	Abundant froth at the commencement.
	48	
	42	
Concentrated sulphuric acid + Hg; with addition of potassic sulphate after complete solution of the earth. Proportion of H_2SO_4 to K_2SO_4 the same as in Gunning's mixture	32	No froth.
	27	
	26	
	25	
The same, without mercury	92	No froth.

The following experiments were made in a flask of 375 c.c. capacity:—

	Minutes.	
Gunning's mixture + Hg	30	Abundant froth.
Concentrated H_2SO_4 + Hg and then K_2SO_4	17	No froth.
Concentrated H_2SO_4 + Hg	65	No froth.

Oxidation thus occurs more rapidly when we add sulphuric acid and mercury, and then, after the solution of the earth, potassic sulphate; it is also accelerated by the use of larger flasks.

The use of mercury requires the addition of potassic sulphide when distilling the ammonia. To do without this addition, I endeavoured to replace the mercury by some other metal.

C.c.	Grms.	Minutes.	
20 H ₂ SO ₄ , without addition, + 18 K ₂ SO ₄		90	
" + 0.3 grm. As ₂ O ₃ + "		60	Abundant froth.
" + 0.5 " Sb ₂ O ₃ + "		70	
" + 1.0 " Sn + "		60	
" + 1.0 " Bi ₂ O ₃ + "		70	
" + 1.0 " MoO ₃ + "		38	Froth disappears rapidly.
" + 1.0 " MoO ₃ + "		35	
" + 1.0 " MoO ₃ + "		33	
" + 3.0 " MoO ₃ + "		30	

It thus appears that molybdic acid offers some advantages over mercury; it makes the addition of potassic sulphide unnecessary, and the time occupied by the oxidation is not increased.

But, on the other hand, the molybdic solution forms a considerable amount of froth on the addition of the potassic sulphate. Further, after oxidation, it is of a strong blue colour, which makes the termination of the oxidation difficult to observe with accuracy. It must also be remembered that commercial molybdic acid frequently contains nitrated impurities. It results from this that although offering certain advantages, molybdic acid does not make a very good substitute for mercury.

Kellner's modification gives fairly rapid results. I made the following trials:—

Kellner's mixture (20 c.c.) + Hg.. ..	{ 45 minutes.
" " " " " "	{ 55 "
" " " " " "	{ 41 "
" " without Hg, with K ₂ SO ₄ ..	50 "
" " " " " "	57 "

The following experiments were made with the view to find the best proportions between the sulphuric acid and the potassic sulphate:—

	Minutes.	
20 c.c. H ₂ SO ₄ + Hg and 7.5 grms. K ₂ SO ₄	41	No froth.
" " " " " "	10.0	" "
" " " " " "	12.5	" "
" " " " " "	15.0	" "
" " " " " "	17.5	" "
" " " " " "	20.0	Rather a lot of froth.
" " " " " "	30.0	Very abundant froth.
" " " " " "	10.0	Very little froth.
" " " " " "	7.5	Hardly any froth.

In the last two experiments the potassic sulphate was added at the commencement of the operation. These figures show that the quantity of this salt to be added varies from 10 to 18 grms.

To sum up, therefore, the best oxidising solution for Kjeldahl's process for the estimation of nitrogen is composed of a mixture of 20 c.c. of concentrated sulphuric acid and from 15 to 20 grms. of potassic sulphate, with the addition of a little mercury.

It is more advantageous to add the potassic sulphate when the solution is complete, but when we have to deal with substances which do not froth it can be added at the commencement of the operation. Under these conditions the liquid becomes colourless after only thirty minutes, but it is advisable to heat it for another quarter of an hour.—*Chemiker Zeitung*, xxii., p. 505.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, February 8th, 1900.

Sir HENRY ROSCOE, LL.D., F.R.S., Vice-President, in the Chair.

THE President, Professor T. E. THORPE, LL.D., F.R.S., delivered the Victor Meyer Memorial Lecture.

Victor Meyer was born in Berlin on September 8th, 1848, and died in Heidelberg on August 8th, 1897. He was at the time of his death President of the German Chemical Society, and had been an Honorary Foreign Member of the Chemical Society since 1883. As a friend of nearly thirty years' standing, and as one who studied with him under Bunsen, the President had acceded to the request of the Council to record its appreciation of the remarkable services Victor Meyer rendered to the science which he cultivated during the all too short period of his activity with such striking assiduity and success.

Some account was given of Meyer in his student days in Heidelberg, of his early connection with the University Chemical Society, and of his work as one of Bunsen's assistants. In 1868 he entered Baeyer's laboratory at the Gewerbeakademie in Berlin, and began the series of half-dozen investigations which characterised his activity during his three years' stay in the German capital. Special reference was made to his memoir on the constitution of the disubstituted benzenes, and upon his method of introducing a carboxyl group into the molecule of aromatic compounds by the action of sodium formate upon the potassium salt of the aromatic sulpho-acids, and it was shown how the results of his observations led to a revision of the views then held with respect to the orientation of the radicals in the "ortho" and "meta" (salicylic) series.

Meyer's success as a private teacher induced von Baeyer to recommend him to Fehling, who sought assistance, especially in the teaching of modern organic chemistry and in practical work in connection with his duties at the Stuttgart Polytechnic. Although he remained in Stuttgart barely a year, he there made one or two discoveries, especially that of the nitro-compounds of the fatty series, which at once stamped him as an original investigator of a very high order. From Stuttgart he was called to Zürich as the successor of Wislicenus, who had been moved to Würzburg, and, when barely 24 years of age, he was elected Ordinarius and Director of the chemical laboratory of the Polytechnic. The thirteen years of Meyer's stay at Zürich constitute the most fruitful and the most brilliant period of his career; before its close he had brought himself within the foremost rank of contemporary investigators. Some idea of his wonderful power of work, and of the stimulus he gave to others, may be gleaned from the fact that during that period the Zürich Laboratory gave close on 130 papers and memoirs to chemical literature. Special stress was laid upon the elaborate investigation of the nitro-compounds of the alkyl series and their derivatives, which continued to occupy Meyer and his pupils for many years. Reference was made to the discovery of the nitrolic and azauric acids, and of the pseudonitroles, and it was pointed out how the characteristic colour reactions afforded by the behaviour of nitrous acid with the primary and secondary nitro-paraffins, and its inability to act upon the tertiary compounds, offered a ready means of distinguishing primary, secondary, and tertiary alcohol radicals. It was shown how the same line of inquiry led to the discovery of the group of the azines and of the ketoximes and aldioximes, and what the influence of these discoveries was upon the stereochemistry of nitrogen.

It was at Zürich that Meyer devised his various methods of determining vapour densities, and it was pointed out

what an important influence the simple and extremely convenient process, known as the air displacement method, has had upon our knowledge of the true molecular weights of substances. Meyer's work on the dissociation of the halogens was especially referred to. Pyrochemical problems, in fact, continued to interest him to the end, and he was quick to take advantage of any hint which seemed to promise the possibility of their solution. In a lecture before the Naturforscher Versammlung, in Heidelberg, he regretted that the lack of vessels of sufficiently refractory material prevented him from working at the higher limits of temperature even then attainable. "There can be no doubt," he said, "that new and undreamt of discoveries will manifest themselves—that a new chemistry will disclose itself—when we are furnished with vessels that enable us to work at temperatures at which water can no longer exist, and at which oxyhydrogen gas becomes an unflammable mixture."

In the autumn of 1882 Meyer was requested to undertake the delivery of the series of University lectures on benzene derivatives which had been interrupted by his friend Weith's death. It was in the course of these lectures that he came upon what is, perhaps, the most brilliant of all his discoveries—that of thiophen. He desired to show his class the indophenin reaction of Baeyer, which, at that time, was held to be indicative of benzene; but, to his astonishment, not a trace of the characteristic blue colour made its appearance, although, as was his wont, he had rehearsed the experiment just prior to the lecture. It happened that his assistant had handed to him a sample of the benzene which had been made in the lecture course by heating benzoic acid with lime, and at once drew his attention to the fact that the rehearsal had been made with the ordinary laboratory supply, which, of course, was derived from coal-tar. It was soon definitely established that it was only coal-tar benzene that gave the indophenin reaction. Meyer's first idea was that it might be occasioned by an isomeric, a second benzene found in coal-tar; but he quickly ascertained that the reaction was due to some sulphuretted product, and that Baeyer's indophenin was a sulphur compound. He found that coal-tar benzene, after repeated shaking with oil of vitriol, no longer reacted with isatin, and it was among the sulphonic acids so formed that he discovered the reactive substance. This he was at first inclined to call *thianthren*, then *thiophan*, next *thiol*, and lastly *thiophen*, to denote that it was a sulphur-containing substance giving derivatives analogous to those of phenyl. Within about six months of his first observation, he was in a position to show to the Swiss Naturforscher Versammlung, by actual preparations, that its chemistry was hardly less extensive than that of benzene itself. In 1888 he published, in the form of a monograph—"Die Thiophengruppe" (Braunschweig: Vieweg u. Sohn)—an account of its condition at that time, from which it appears that, during the preceding five years, no fewer than 105 contributions to its history had been made from his own laboratory, and some 40 from those of others.

On the death of Hübner, Meyer received a call to Göttingen, which he accepted, and where a new laboratory was to be built for him. Here he continued his pyrochemical work, and his investigation of the thiophen derivatives, and began with Paul Jacobson the admirable "Text-book of Organic Chemistry," which, in the critical selection and arrangement of its material, is unsurpassed. With Auwers, he resumed the study of benzil and its derivatives, which he had begun with Wittenberg and Goldschmidt, and with Münchmeyer he commenced the study of the behaviour of phenylhydrazine towards various groups of oxygen compounds. With Demuth, he undertook the investigation of the sulphuranes. Other notable papers of this period were on isophthalaldehyde; on the negative nature of the phenyl group; on the thio-derivatives of deoxybenzoin and its analogues (desaurins); and with Riecke on the carbon atom and valency.

Stereochemical questions—we owe the phrase to Meyer—occupied much of his thought at this period. His perspicacity and insight are well illustrated in the lecture he gave to the German Chemical Society, in 1890, on the results and aims of stereochemical research. It is of interest to the student as giving a fairly complete historical account of the development of space formulae, and more especially for the criticism of the work of Baeyer and Wislicenus on the stereochemical formulæ of single-, double-, and treble-linked carbon compounds, and of the stereochemical conceptions of Hantzsch and Werner in the case of nitrogen compounds. To this period belongs also his work on the aromatic nitriles, on tetramethylsuccinic acid, and on the oximes of phenanthraquinone.

Meyer was not destined to remain long in Göttingen. The new laboratory was barely finished when, in 1889, he received a call to Heidelberg, as successor to Bunsen. To Heidelberg accordingly he went with the coveted title of Geheimrath and the promise of a new and enlarged laboratory. Although only 40 years of age, he was now, so far as worldly position was concerned, at the summit of his career. In conjunction with a number of his pupils he began the investigation of the conditions determining both the gradual and the explosive combustion of gaseous mixtures, notably of electrolytic gas, and of the simpler hydrocarbons with oxygen. In the case of mixtures of aliphatic hydrocarbons with equivalent amounts of oxygen, it appeared that the temperature of explosion falls as the number of the carbon atoms in the molecule increases; that it is probably lower for primary than for corresponding secondary hydrocarbons; and is less for hydrocarbons containing a double bond than for those containing only single bonds, and is still less for those containing a triple bond.

In 1892 Meyer and Wachter announced the existence of the iodoso-compounds, a series of aromatic derivatives in which the monovalent group IO replaces hydrogen. The study of these compounds led to the discovery of the remarkable substances known as the iodonium bases—compounds in which two of the valencies of the trivalent iodine atom are satisfied by aromatic radicles, while the third is satisfied in the free base by hydroxyl, and in the salts by an acid radicle. The iodonium bases are readily soluble in water, are strongly alkaline, and in their behaviour, as in that of their salts, show a remarkable similarity with the derivatives of silver, lead, and more particularly thallium.

Reference was also made to the study of the conditions determining the formation and hydrolysis of ethereal salts of aromatic acids, which occupied Meyer, in conjunction with his pupils, and more especially Sudborough, from 1894 up to the year of his death.

Meyer contributed to the literature of chemistry, either alone or in conjunction with his pupils, upwards of 300 memoirs and papers.

As the director of a large chemical laboratory, and as a laboratory teacher, Meyer worthily followed in the footsteps of Bunsen. He was an admirable lecturer, clear, vigorous, and extremely lucid, and his lectures were most popular. As a teacher, he had a wonderful faculty of infusing enthusiasm into his students. His literary ability, combined with his power of exposition, made him an admirable writer of popular science articles. His merits were recognised in every land where science is cultivated, and he was an Honorary Member of many Continental academies. The Royal Society awarded him the Davy Medal in 1891, and in the spring of that year he attended the celebration of the Jubilee of the Chemical Society, and the eloquent words which he uttered in responding to the toast of "Our Foreign Members" will not readily be forgotten by those who attended the banquet on that occasion.

On the motion of Professor DEWAR, seconded by Dr. ARMSTRONG, a vote of thanks was passed to the President for his lecture.

Ordinary Meeting, February 15th, 1900.

Professor THORPE, F.R.S., President, in the Chair.

MESSRS. J. Dewhirst, Edgar M. Chapman, and Thomas A. Henry were formally admitted Fellows of the Society.

It was announced that the following changes in the Council were proposed by the Council:—

As *Vice-Presidents*—Professor Divers, M.D., F.R.S., and Dr. T. Stevenson, *vice* Professor Ramsay, F.R.S., and Professor Emerson Reynolds, F.R.S.

As *Ordinary Members of Council*—Dr. Chattaway, Professor Collie, F.R.S., Professor Augustus Dixon, M.D., and Mr. W. J. Pope, *vice* Mr. Bevan, Dr. Moody, Dr. H. F. Morley, and Professor Smithells.

Certificates were read for the first time in favour of Messrs. Alexander William Bain, 2, Muswell Rise, Highgate, N.; Arthur Charles Davis, 3, Vinery Road, Cambridge; Noel Fielding Deerr, 26, South Parade, Chelsea, S.W.; Adolf Liebmann, 10, Marsden Street, Manchester; Frederick Thomas Munton, The Oak House, Winsford, Cheshire; James Wallace Sandford, Adelaide, S.A.; Bertram D. Steele, 40, Herndale Road, London, S.W.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Frederick Nolan Baker; Alexander Hutcheon Bennett; Sidney Calvert, M.A., B.Sc.; Oscar Joseph Cole, B.A.; William Francis Cooper, B.A.; Thomas Cuthbert Davison; Harry M. Dawson, B.Sc., Ph.D.; Stephen M. Dixon, B.A.; Alexander Findlay, M.A., B.Sc.; James Foulds; Granville Reginald Gee; Julius Geldard; Robert W. Gray; Alfred William Harvey; Herbert William Hart; Adam Houston; Henry William Hutchin; Henry Jackson, B.A., B.Sc.; Thomas Goode Joyce, B.Sc.; W. C. Robert Kynaston; Arthur Robert Laws; Thomas Ebenezer Mackenzie; William Mair; A. W. Cranbrook Menzies, M.A., B.Sc.; J. L. Rutgers Morgan, M.A., Ph.D.; Edgar Ford Morris, M.A.; Herbert Newall Morris; Ernest Brooks Naylor, B.Sc.; James Fraser Readman; Walter A. Riley; James McConnell Sanders; Fred. Pilkington Sargeant; Edward Shrapnell Smith; James Hart-Smith; Bertram Vincent Storr, B.Sc.; Archie Hugh Strong; Gustavus A. Waterhouse, B.Sc.; Leonard Philip Wilson.

Messrs. A. W. Crossley, F. J. M. Page, and E. W. Voelcker were appointed to audit the Society's accounts.

Of the following papers, those marked * were read:—

*17. "*Ammonium Amidosulphite*." By EDWARD DIVERS and MASATAKA OGAWA.

When dry enough, ammonia does not combine with sulphur dioxide at a low temperature. When less dry, it does so, with such rise of temperature that the product of the union is at once partly decomposed. But by dissolving the ammonia in dry, alcohol-free ether, and passing the sulphur dioxide into the solution, kept very cold, the product is precipitated undecomposed. It is colourless, very deliquescent, and unstable in the air. It dissolves in water with a hissing sound, and, when the water has been well cooled, yields a solution which gives the reactions of ammonium sulphite only. It is also very soluble in absolute alcohol, forming the salt lately described by the authors, ethyl ammoniumsulphite. It is formed from 2 mols. ammonia and 1 mol. sulphur dioxide. In a dry atmosphere, at temperatures such as 35°, it loses nearly half of its ammonia, as well as a little water. After the decomposition, no sulphite-forming substance remains, and the mass is somewhat orange-coloured from the presence of a very small quantity of a red substance. A very little sulphate is also present, but the residue consists mainly of substances the composition and nature of which are not yet fully determined. They seem to be thio-amido-sulphonic compounds, as yet unknown, which, by heat, by spontaneous partial hydration, or by treatment with ammonia in alcoholic solution, yield sulphur, sulphur dioxide, sulphate, thiosulphate, amidosulphate, imido-

sulphate, and, almost certainly, sulphamide; when dissolved in water they give a reaction with silver nitrate, closely resembling, yet not that of a trithionate, for when acidified, their solution gives no sulphur or sulphur dioxide, or only mere traces, until it has been heated under pressure or for a long time.

The undecomposed salt appears to be correctly named *ammonium amidosulphite*, and to have the formula $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}_4$. The preparation of this salt shows Rose's assertion, that the gases unite only in equal volumes forming an orange substance which at once decomposes with water into sulphate and trithionate, to be altogether wrong and to be due to his having failed to prevent the decomposition of the product first formed.

*18. "*On the Products obtained by Heating Ammonium Sulphites, Thiosulphate, and Trithionate*." By EDWARD DIVERS and MASATAKA OGAWA.

The authors have ascertained that *anhydrous ammonium sulphite* and *pyrosulphite* sublime unchanged at about 150° in a current of dry nitrogen, the vapours being no doubt the dissociated gases. At a temperature somewhat higher, *ammonium trithionate* decomposes into sulphur dioxide, sulphur, and ammonium sulphate. At about 150°, *ammonium thiosulphate* decomposes almost entirely, leaving a residue of sulphur and giving a sublimate of anhydrous ammonium sulphite; very small quantities of ammonia and hydrogen sulphide are also given off, giving rise possibly to a trace of trithionate. According to Spring, ammonium thiosulphate sublimes unchanged, except for temporary dissociation. To obtain the above results, moisture must be absent: the effect of slowly heating *hydrated ammonium sulphite* in a current of dry nitrogen is partly to dehydrate it, partly to convert it into pyrosulphite, at about 120°; and then at about 150°, the residue decomposes into sulphur dioxide and ammonium sulphite (approximately hemihydrated) which sublimes.

Ammonium trithionate, a very deliquescent and unstable salt, not hitherto described, was prepared from the potassium salt by the use of hydrofluosilicic acid and ammonia, being much too soluble to admit of preparation by Plessy's process for the potassium salt. *Ammonium sulphite* was conveniently precipitated by saturating its concentrated solution with ammonia in a cooling mixture, and the *pyrosulphite* by similarly saturating its solution with sulphur dioxide. *Anhydrous ammonium sulphite* was obtained by exposing the hydrated salt in a desiccator over potash in an ammoniacal atmosphere.

*19. "*The Colour of Alkali Nitrites*." By EDWARD DIVERS.

As Boguski (*Z. Russ. Chem. Soc.*, 1899, xxxi., 543) has published his observations that a solution of sodium nitrite had a slight yellow colour which he could not remove, and which he attributes to the presence of an impurity, the author wishes to recall attention to his own statement (*Trans.*, 1899, lxxv., 86) that alkali nitrites have a slight yellow colour, especially in solution, and to Groves's statement in denial of its accuracy (*Proc.*, 1898, xiv., 222). The author desires now to claim accuracy for his own statement. The colour of the potassium salt is much more manifest than that of the sodium salt, principally because of its ability to yield exceedingly concentrated solutions. Solutions of potassium nitrite three parts of salt in one of water, are strongly yellow, particularly when thoroughly free from turbidity. Solutions of equal strength are equally coloured, whatever has been the source of the nitrite. Alkali nitrites are yellow in the fused state. The author is confident that Boguski's promised endeavour to remove the colour of sodium nitrite will be as futile as were those of chemists, long years ago, to remove the pink colour from manganous salts. Boguski's observation that the solid nitrite is sometimes apparently without colour, depends upon the well known optical effect of fine division in lessening the colour of transparent solids.

*20. "Solubility of Mixed Potassium Nitrite and Nitrate." By EDWARD DIVERS.

By crystallising out, as far as possible, the nitrate which is mixed with potassium nitrite in its usual method of preparation, there remains a mixture of about three parts of nitrite to one part of nitrate, and this constitutes the ordinary nitrite of commerce. This mixture is soluble in one-fourth its weight of water, although the pure nitrite requires one-third of its weight, and the pure nitrate about four times its weight of water to dissolve it. Accordingly, when a solution of three parts pure potassium nitrite in one part water is digested with powdered potassium nitrate at the common temperature, it readily dissolves up one part of this salt.

DISCUSSION.

In reply to remarks by Messrs. Baker, W. P. Bloxam, and Scott, Dr. DIVERS said that the ammonium amidosulphite rapidly deliquesced in air, and he quite agreed with Mr. Bloxam's observation as to the great activity of hydrated ammonium sulphite with regard to atmospheric oxygen. As Rose had taken no precautions to maintain a low temperature during the reaction, there was no doubt that the compound resulting from the combination of two volumes of ammonia with one of sulphur dioxide gave off half of its ammonia again under the influence of the high temperature produced in the reaction.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, February 23rd, 1900.

Prof. S. P. THOMPSON, F.R.S., Foreign Secretary, in the Chair.

PROF. R. W. WOOD, of the University of Wisconsin, U.S.A., exhibited and described:—

1. *Photographs of Sound Waves and the Kinematographical Demonstration of the Evolutions of Reflected Wave fronts.* The sounds were produced by electric sparks and photographed by means of the light emitted by carefully timed subsequent sparks, according to the method described in the *Phil. Mag.* for last year. The photographs included:—

- The reflection of a spherical wave, as a spherical wave from a plane surface.
- The reflection by an ellipse of circular waves from one focus, and the concentration of the waves as circular waves at the other focus.
- The plane wave-front formed by the reflection of a spherical wave at a parabolic surface.
- The wave-front formed by a spherical wave incident on a spherical surface.
- The wave-front formed by a plane wave incident on a spherical surface.

In cases (d) and (e) the wave-fronts are complicated and contain cusps. Prof. Wood pointed out that the paths of the cusps on the wave-fronts traced out the caustic curves.

In the following cases the wave-fronts were drawn for one hundred successive positions, and the evolution of the reflected wave was made clear by means of a kinematograph:—

- Plane wave on a hemispherical mirror.
- Spherical wave on a hemispherical mirror, and—
- Circular wave inside a complete circular mirror.

2. *A New Soudoscope.*—In this instrument the real and inverted images formed by two convex lenses are viewed stereoscopically. The inversion of the object viewed causes the relief to be reversed.

3. *Diffraction Colour photographs.*—Prof. WOOD showed some coloured photographs taken by his diffraction process. The principle of the method is based upon the tri-colour theory. Different colours are produced by gratings so ruled and arranged as to throw upon the eye

the particular constituents of the required colours. The arrangement of gratings necessary to produce a coloured picture is obtained by photographing properly spaced gratings through red, green, and blue chromograms of the object. The superposition of one grating upon another, which occurs in this process, gives rise to an in-and-out-of-step arrangement, which produces secondary spectra. These, however, seldom affect the picture to any serious extent.

4. *Artificial Parhelia.*—When printing fine gratings upon gelatin, if the film is too thick, no print is formed, but the gelatin warps. If such a film is placed in a converging beam, the central image is accompanied by four marked concentrations of light situated at the extremities of two diameters at right angles. An examination of one of these plates with a microscope shows that there is a ridge for every third line of the grating, and that the plate is crossed at right angles to these lines by irregularly spaced cross ridges.

Prof. WOOD also exhibited some photographs taken by zone plates, a silvered copy of a Rowland grating, a photograph of a dynamite explosion, the motion of a ball in its flight, and the anomalous dispersion produced by a cyanine prism.

Mr. BOYS gave some details concerning the photograph of the explosion shown.

Prof. EVERETT expressed his interest in the demonstrations.

Prof. HERSCHEL asked if the photographs of sound waves after reflection had been verified by comparison with waves on mercury.

Mr. WATSON pointed out that this could not be done, as it is impossible to get a solitary wave on the surface of mercury. Owing to the dependence of velocity on wave-length, any such solitary wave draws out into a train of waves.

The CHAIRMAN proposed a vote of thanks to Prof. WOOD, and announced that, by invitation of Prof. Callendar, a Special Meeting will be held in University College on March 2nd. The Meeting then adjourned.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, February 20th, 1900.

Prof. HORACE LAMB, M.A., F.R.S., President, in the Chair.

"Some Criticisms on the Modern Theory of Solutions."

By EDGAR F. MORRIS, M.A.

By applying the ordinary assumptions of the kinetic theory of solutions to the case of a semipermeable cell depressed below the surface of the solvent, the result is deduced that the percentage composition of any solution is a linear function of its density. The form of the reaction equation for the catalysis of esters shows that the action cannot be attributed to independently moving ions. Other facts disproving this theory are the occurrence of electrolytic solutions with normal molecular weights, and of cases where the molecules would have to be regarded as split into most curious fragments to provide a sufficient number of ions—in the case of certain metals in mercury solution into more ions than atoms. Prof. Fitzgerald has previously shown the physical basis of this theory to be unsound, and, as the chemical applications give untrue results, it would appear to be time to abandon the theory.

Borates of the Magnesium Series.—L. Ouvrard.—

The author's experiments lead him to believe that the methods used (by the wet way) for preparing definite tri-basic borates are not satisfactory, owing to the easy decomposition of the borates by water. If, however, the same borates are prepared by the dry method, which the author describes, the body prepared presents in general a great amount of stability towards various agents of decomposition.—*Comptes Rendus*, cxxx., No. 6.

CORRESPONDENCE.

LAW OF ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—If the process of arranging the elements according to the law discovered by Prof. Delaunay, and described in a letter to the CHEMICAL NEWS (vol. lxxxi., p. 70), is continued, the addition of the atomic weights of the several pairs of elements gives the series:—

$$\text{Na} = 23.05, \text{K } 39.11, \text{Cu } 63.6, \text{Rb} = 85.43, \text{Ag} = 107.92.$$

A somewhat curious relation is to be noticed between the atomic weights of these elements, for by adding the atomic weight of sodium to that of any other in the series a number is obtained which approximates to the atomic weight of the next element in the series, thus:—

$$\text{Na} + \text{K} = 23.05 + 39.11 = 62.16 = \text{Cu} - 1.44$$

$$\text{Na} + \text{Cu} = 23.05 + 63.60 = 86.65 = \text{Rb} + 1.22$$

$$\text{Na} + \text{Rb} = 23.05 + 85.43 = 108.48 = \text{Ag} + 0.56$$

I should like to point out an error which occurs in Prof. Delaunay's third list; Cr is left out, and should occupy the place of V, and V the place of Ti (in brackets) in his list.—I am, &c.,

NEMO.

NOTICES OF BOOKS.

The Chemistry of Vegetation and Agriculture. ("Chimie Végétale et Agricole"). By M. BERTHELOT, Senator, Permanent Secretary of the Academy of Science, &c. In Four Volumes. Paris: Masson et Cie. 1899. Pp. 1997.

SYNTHETICAL chemistry, which has occupied M. Berthelot's attention to such a great extent since the year 1853, effects in the laboratory what plant-life does in the field. The author effected the synthesis of the carbides of hydrogen and the alcohols, by starting from carbonic oxide, carbonic acid, and water,—that is to say, the simple mineral compounds which are acted on by vegetable organisms.

In 1860, when the author published the general methods by which he had attacked and overcome the problem of purely chemical synthesis, he also pointed out the importance of biological synthesis,—that is to say, synthesis carried on under conditions compatible with the natural phenomena of life. The realisation of these ideas was reached when a portion of the estate of the Chateau of Meudon was placed at his disposal in 1883. The results obtained at this experimental station have been published year by year, and the details of the experiments and the analyses made have been given in the *Annales de Physique et de Chimie*. The time has now come to collect all these scattered notes and papers in one publication, setting forth the whole co-ordinated system.

The fundamental principle of these experiments has turned on the study of the fixation of the free nitrogen of the atmosphere by the soil and by vegetation, under the influence of the micro organisms present, and under the action of the silent atmospheric electricity.

The discoveries made by the author in this respect have wrought a great change in the ideas held by the best authorities on the negative rôle of the free atmospheric nitrogen in vegetation. Thirty years ago free nitrogen was not considered to have any influence on vegetation or agriculture, but this opinion has since been entirely altered. He shows, by experiments spreading over seven years on sterile soil (that is, deprived of microbes), such as argillaceous sand, and then true vegetable mould, that certain of these sterile soils have the power of fixing ni-

trogen, as well in the absence of higher vegetable life as with its help. The influence of leguminosae on the fixation of nitrogen, so long affirmed by M. George Ville, though not then accepted, has been confirmed and explained by M. Berthelot's discoveries with regard to the microbes in the soil and their action in the mechanism of the assimilation of nitrogen. The sum of these various discoveries constitutes a new doctrine, but there is also a third cause of the fixation of nitrogen, and this is a purely chemical one.

These are the questions which are dealt with in vol. I.

The second volume contains the author's researches on the general progress of vegetation, which gives a sort of ponderable chemical equation of an annual plant during the whole of its evolution, from its first sowing up to the time when it reproduces the seed at the end of its development: this subject has not previously been dealt with systematically, in spite of its importance.

Volume III. is on special researches on vegetation and its products; in it the author examines the presence and distribution of certain special elements in plants, such as sulphur, phosphorus, silica, &c.; the formation of oxalic acid and carbonates; the formation and partition of nitrates in vegetation; and the emission of carbonic acid and absorption of oxygen by the detached leaves of plants. He then treats of the decomposition of sugars by purely chemical means, with the production of carbonic acid, &c. A special part of this volume consists of the experiments and observations made at various times on the definite principles having the double power of combining with free oxygen and then giving it up to bodies which oxygen will not oxidise directly—a phenomenon connected with both oxidising ferments and the microbial fixation of nitrogen.

Volume IV. contains two distinct parts, the one general, relating to soils, their composition, &c., and the other relating specially to wine, and the influence of soils on its bouquet.

It is not only the chemical and biological side of the question that is dealt with in so masterly a manner in this work, but also the practical side by which these phenomena can best be adapted and applied to agriculture and its allied industries, to the advantage and profit of mankind.

This is a wide and important subject, and will demand very serious attention before many years have passed over our heads.

First-stage Magnetism and Electricity: treated from the Stand-point of Potential and Potential-gradient. By R. H. JUDE, M.A., D.Sc. With 138 Illustrations. London: W. B. Clive, University Correspondence College Press. Pp. 350.

It has often been noticed by teachers, as well as by examiners, that one of the greatest difficulties met with by students is the conception of "Electrical Potential." The difficulty lies not in the mathematical aspects of the subject, but in attempting to apply the idea of potential to the general explanation of electrical phenomena. In the opinion of the author the trouble arises from two causes; viz., that the idea of potential is not brought before the student until too late, and from the fact that man has no "electrical sense," such as he has of heat, sound, light, &c. The object of this book is to overcome both these difficulties. The notion of potential is brought before the student very early in the course, so that he may the more easily assimilate and become accustomed to it. This subject, and electrostatics in general, form Part I. of this volume; in Parts II. and III. the aim of the author has been to set forth the fundamental principles of electrodynamics and magnetism as clearly as possible: in this he has succeeded, and has given us a book which will no doubt be fully appreciated by beginners in electrical science. A number of exercises and examination papers are included in the volume, but there is one point which

might be improved: the author is a great deal too fond of italics; in fact, there is not a page on which this form of emphasis is not used several times.

Richter's Organic Chemistry, or Chemistry of the Carbon Compounds. Edited by Prof. R. ANSCHÜTZ. Authorised translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American, from the Eighth German Edition. Vol. I. *On the Aliphatic Series.* With illustrations. London: Kegan Paul, Trench, Trübner, and Co., Lim. 1899. Pp. 625.

As the second edition was a great improvement on the first, so does the third show a great advance beyond the second. Indeed, the book is very different from the earlier editions, and has undergone many radical changes.

The marvellous advances in the various lines of synthetic organic chemistry have made it necessary to effect considerable changes in the text, and it has been found better for practical reasons to issue this new edition in two volumes.

Volume I. "On the Chemistry of the Aliphatic Series," is divided into eight parts, beginning with the hydrocarbons, their halogen derivatives, the oxygen derivatives of the methane hydrocarbons, and successively, the mono-, di-, tri-, tetra-, penta-, hexa-, and polyhydric alcohols and their oxidation products.

The work is well and clearly printed and provided with an excellent index of 36 pages of two columns each.

Volume II. is in rapid preparation, and will be published shortly.

Handbook of Chemical Analysis. ("Manuel d'Analyse Chimique"). Applied to the Examination of Industrial and Commercial Products. By EMILE FLEURENT. Paris: G. Carré and C. Naud. 1898. Pp. 582.

This work does not pretend to be a complete treatise on chemical analysis, but a practical handbook, destined to serve as a guide to those engaged with commercial chemical products. The author has endeavoured to realise three special objects; to describe, without overburdening them with theoretical details, the general methods of qualitative and quantitative inorganic analysis, and elementary organic analysis; to simplify the examination of materials and to save time, by only giving one or two methods by which the results can be rapidly obtained; and to collect together in one volume the methods of examination of the most important, as well as the most diverse products, both metalloids and metals, chemical and organic manures, vegetable and animal products, fermented drinks, &c., &c.

Numerous tables are given at the end of each chapter giving in a practical form the results obtained by applying the methods described in the text.

Outlines of Theoretical Chemistry. By LOTHAR MEYER, Professor of Chemistry in the University of Tübingen. Translated by P. P. BEDSON, M.A. (Dun.), D.Sc. (Lond. and Dun.), F.C.S., &c.; and W. C. WILLIAMS, B.Sc., F.C.S., &c. Second Edition. London, New York, and Bombay: Longmans, Green, and Co. 1899. Pp. 240.

In this work the author has abstained from giving numerical results of observations and measurement, or detailed descriptions of experimental methods, but has confined himself as far as possible to theoretical speculations which, though of value to the student, are also of interest to those who, not wishing to be troubled with details of investigations, are anxious to become familiar with the general conclusions arrived at. Though retaining the original form of the first edition, this, the second edition, has been brought up-to-date, by footnotes and appendices.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 6, February 5, 1900.

Superficial Tension of some Organic Liquids.—Paul Dutoit and Louis Friderich.—The authors have measured the temperature coefficient of superficial molecular energy of a group of organic liquids. This research verified the relations found by Ramsay and Shields between the coefficient of temperature and the molecular weight of the liquid. The authors find that—(1) The coefficient of temperature varies with the temperature for liquids which do not retain the same molecular size during the interval of temperature under consideration; (2) this coefficient is independent of temperature for normal liquids; (3) for normal liquids this coefficient does not represent a single constant for all bodies, but varies between certain indefinite limits, which have not yet been determined. With regard to the two first points, the authors' results confirm those published by Ramsay and Shields.

Volumetric Estimation of Hydrogen and Chemical Tensions.—Alb. Colson.—Oxide of silver has the power of absorbing hydrogen without acting either on the saturated carbides or on oxygen. M. Fouqué, in his researches on volcanic gases, separated the hydrocarbides from hydrogen by shaking up the gas with alcohol and dissolving the carbides. The author proposes an inverse method; since this latter is independent of the coefficient of solubility. Oxide of silver behaves as it emitted vapours in hydrogen at all temperatures, and as if hydrogen acted principally on these vapours. The author's experiments show the mechanism of diffusion of solids in gases.

Action of Concentrated Ammonia on Mercuri-ammonium Iodide.—Maurice François.—Dimercur-ammonium iodide, otherwise called tetramercur-ammonium iodide, is produced when mercuric iodide is heated with a large excess of concentrated ammonia. The reaction is represented by the equation $2\text{HgI}_2 + 4\text{NH}_3 + \text{H}_2\text{O} = 3\text{NH}_4\text{I} + \text{Hg}_2\text{NIH}_2\text{O}$. The dimercurammonium iodide is insoluble, and remains suspended in the solution of ammonium iodide. By studying this reaction, the author finds that it is limited and reversible. At the moment of equilibrium, a given volume of the ammoniacal liquor contains a quantity of free ammonium iodide, which is constant for a given temperature and for a given concentration of ammonia.

Acidimetric Value of Substituted Malonic Acids compared with those of corresponding Normal Diacids.—G. Massol.—The author determines numbers under identical experimental conditions with those under which similar numbers of the diacids were determined; he compares them, and draws the following conclusions:—(1) For normal acids of the oxalic series increase of molecular weight leads at first to a progressive diminution of the acidimetric value, corresponding to about 2 cal., then to 1 cal., for each CH_2 added. (2) For the homologous series of mono-substituted malonic acids the phenomenon is identical; the quantity of heat evolved decreases at first with increase of molecular weight, then remains constant. In this case, however, the minimum is sensibly higher than in the former series. (3) If each mono-substituted acid is compared with its normal homologue containing the same number of atoms of carbon—and having, consequently, the same molecular weight—it is found that the abnormal acid evolves more heat than the normal. (4) These results confirm the conclusion, which the author has already announced, that the acidimetric value of polyacids depends much more on their molecular structure and

the separation of the carboxyls than on their molecular weight.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 22.

Properties of Calcium.—Henri Moissan.—Already inserted.

Preparation of Lithium-ammonium, Calcium-ammonium, and of the Amides of Calcium and Lithium.—Henri Moissan.—When liquid ammonia cooled to -50° is brought into contact with calcium or lithium an intensely blue coloured solution is produced. The methodical study of the properties of calcium led the author to examine the reactions produced by calcium in the presence of gaseous and liquid ammonia. Wishing to find the temperature limit at which the alkaline ammoniums could be formed, he experimented with the four metals potassium, sodium, lithium, and calcium. Each metal was placed in a U-tube connected with a supply of dry ammonia gas; these were placed in a water-bath; for low temperatures, the water was replaced by acetone and the temperature diminished by adding small pieces of solid carbonic acid; in this way the temperature could be brought down to -75° , and the ammonia gas solidified. In these experiments the ordinary atmospheric pressure was always maintained. The following results were obtained:—

Lithium is attacked at $+70^{\circ}$ with liquefaction.	
Calcium " " $+20^{\circ}$ without "	
Potassium " " -2° with "	
Sodium " " -20° with "	

These figures also represent the temperatures of decomposition of the ammonium metals at the ordinary pressure in a current of ammonia gas. To establish the composition of lithium-ammonium, two methods were followed. Experiments I. and II. were made by starting with a known weight of the metal, and weighing the ammonia combining with it; Nos. III. and IV. were obtained by preparing lithium-ammonium as described above, and estimating the ammonia by Schloesing's method.

	I.	II.	III.	IV.	Theory for NH_3Li .
Lithium . .	28.07	28.40	28.72	28.82	29.16
Ammonium ..	71.93	71.60	71.28	71.18	70.83

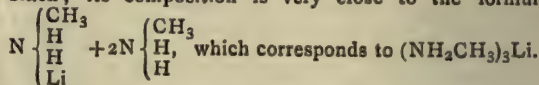
The composition of calcium-ammonium was found by similar means; Nos. I., II., and III. by synthesis, and No. IV. by estimating the calcium and the ammonia in a known weight of the compound.

	I.	II.	III.	IV.	Theory for $(\text{NH}_3)_2\text{Ca}$.
Calcium . .	37.04	37.60	37.41	37.44	37.03
Ammonium ..	62.96	62.40	62.59	62.51	62.96

Action of Acetylene on the Ammonium Metals.—Henri Moissan.—When we cause the alkaline metals to react on the different carbides of hydrogen and on organic compounds, the decomposition is often very violent. As soon as the temperature rises, complicated phenomena of polymerisation and hydrogenation intervene, and soon hide the principal reaction, but the facility with which the ammonium metals form compounds at a low temperature gives us a new method with a much slower reaction. After fully describing the apparatus and the manipulatory details, the author describes the action of acetylene, of sodammonium, potassammonium, lithium-ammonium, and calcium-ammonium, by which he obtained the following acetylenic acetylides:— $\text{C}_2\text{K}_2\text{C}_2\text{H}_2$, $\text{C}_2\text{Na}_2\text{C}_2\text{H}_2$, $\text{C}_2\text{Li}_2\text{C}_2\text{H}_2 \cdot 2\text{NH}_3$, $\text{C}_2\text{Ca}_2\text{C}_2\text{H}_2 \cdot 4\text{NH}_3$.

Preparation and Properties of an Organic Ammonium: Lithium-monomethylammonium.—Henri Moissan.—When methylamine is passed over metallic lithium at -20° , it condenses and wets the metal; abundant blue striæ are formed, and the temperature rises; the metal soon disappears, leaving a blue liquid. When

the solution is complete, an excess of methylamine is allowed to condense, and the current of gas then cut off, the tube is taken out of the refrigerator, and allowed to take the temperature of the laboratory. The product is then very thick and of a dark blue colour, approaching black; its composition is very close to the formula



Colour of Carbide of Calcium.—Henri Moissan.—Already inserted (see p. 67).

The Preparation and Properties of Crystallised Phosphide of Calcium.—Henri Moissan.—Already inserted (see p. 87).

Heat of Formation of Quicklime from its Elements.—Henri Moissan.—Already inserted (see p. 89).

Preparation of the Arsenides of Strontium, Barium, and Lithium in the Electric Furnace.—P. Lebeau.—Already noticed in this column (vol. lxxx., p. 59).

Speed and Limit of Etherification of Phosphoric Acid by Glycerin.—H. Imbert and G. Belugou.—The return of glycerophosphoric acid when we add with more or less hydrated phosphoric acid on glycerin at various temperatures, depends principally, not only on the state of hydration of the acid and the temperature, but also on the time.

Salicylic and Paraoxybenzoic Aldehydes and Salicylhydramine.—M. Delépine and P. Rivals.—Already noticed (vol. lxxx., p. 295).

Metallic Derivatives of Salicylhydramide.—M. Delépine.—The author is of the opinion that the most logical way of expressing the constitution of the salicylhydramides is by making them derivatives of the salicylimides, of which Schiff has described the cupric compounds of the type $\text{Cu} \begin{Bmatrix} \text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{R} \\ \text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{R} \end{Bmatrix}$. Methyl-

salicylimide of copper is obtained by adding an alcoholic solution of acetate of copper in methylamine to an alcoholic solution of salicylic aldehyde. An emerald-green precipitate is formed, crystallising in needles; re-crystallisation in alcohol enables the methylsalicylimide to be obtained in dark green, almost black, crystals, several c.m. long. On analysis it gave 19.29 per cent of Cu.

Heat of Oxidation of Tungsten.—M. Delépine and L. A. Hallepeau.—Already inserted (see p. 66).

On the Symmetric Dinitrodixyl- and the Dinaphthyl-Carbamides.—H. Vittenet.—Two molecules of nitro-5-oxylidine-1:3:4 and one molecule of COCl_2 in toluene at 20 per cent was heated for an hour in a sealed tube at 130° . A brown mass was obtained, which was washed with cold benzene, then warm water; it was then crystallised in acetic acid. Analysis gave $\text{N} = 15.58$. Another body, containing $\text{N} = 15.74$, was obtained in a similar manner by heating two molecules of nitro-6-oxylidine-1:3:4 in the same way.

On Chloracetate of Phenyl and its Reactions.—A. Morel.—The author describes the preparation of chloracetic ethers, and the action of alcohols and of ammonia on chloracetate of phenyl. NH_3 reacts on the phenolic ether function to give an amide before reacting on the alcoholic chloride function to give an amine; it was also noticed that alcohol very rapidly transforms

$$\begin{array}{ccc} \text{CH}_2\text{Cl} & \text{into} & \text{CH}_2\text{Cl} \\ | & & | \\ \text{COOC}_6\text{H}_5 & & \text{COOC}_2\text{H}_5 \end{array} \quad \text{in a sealed tube at } 130^{\circ}.$$

Reactions of Chloracetate of Phenyl and Glycolate of Phenyl.—A. Morel.—The comparison between the reactions of the monochlorated chloride of acetyl, of chloracetate of benzenol, and of the double glycolate of benzenol on the one hand, and of oxychloride of carbon, chlorocarbonate and neutral carbonate of benzenol on the other hand, show that these two groups belong to

two different classes. The first are clearly derived from a body of complex functions, the second from a symmetric body.

Cyclic Isomerisation of Methyloctanedienonol.—G. Leiser. — The product of condensation of methylheptenone with formic ether may be regarded as a body with an aldehydic function, methyloctenonal, $\text{CH}_3 > \text{C} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{CH}_2 - \text{CHO}$; or, as its tautomer, the secondary incomplete alcohol, methyloctadienonol, $\text{CH}_3 > \text{C} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{CH} = \text{CH} - \text{OH}$.

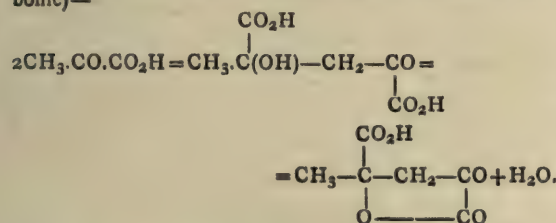
The author added 60 grms. of the latter to 300 grms. of sulphuric acid at 80 per cent, and agitated until dissolved. There was no sensible heating, but only a brown colouration of the liquid. The whole was boiled for a few minutes on the water-bath, then cooled and diluted with water; the citron odour has disappeared and given place to a faint but agreeable smell. The aqueous solution is extracted with ether; the ethereal layer, washed with water, is distilled. At 115–117°, under 17 m.m., a liquid is isolated; analysis shows it to be an isomer of methyloctadienonol, $\text{C}_9\text{H}_{14}\text{O}_2$.

On the Aminocampholenes.—E. Blaise and G. Blanc.—Already noticed (see vol. lxxx., p. 72).

Apparatus for the Estimation of Carbonic Acid in Mineral Waters.—A. Held.—This paper requires the accompanying diagram.

MISCELLANEOUS

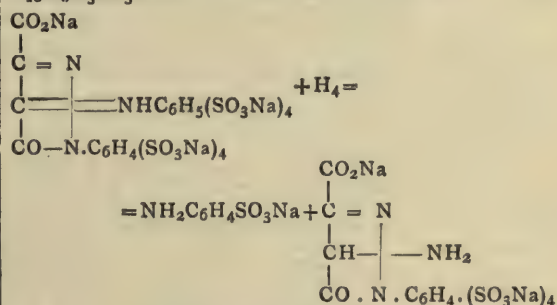
On Parapyruvic Acid.—L. Wolff.—The pyruvates in aqueous solution slowly undergo a modification and become transformed into the so-called syrupy salts of pyruvic acid. This was known by Berzelius and Voelckel. This modification is much more rapid in the presence of traces of certain condensation agents (CNK, KOH, NH_3), and leads to the transformation of neutral salts of a bibasic acid, $\text{C}_6\text{H}_8\text{O}_6$. This acid, which may be called pseudo-pyruvic, results from the condensation of 2 molecules of pyruvic acid; but in the free state it partly splits up into water and lactonic acid, $\text{C}_6\text{H}_6\text{O}_5$ (keto-valerolactonecarbonic)—



As for the free pyruvic acid, it also undergoes a transformation. Whether the modified acid contains the same mixture has not yet been proved, but a crystallisable acid, $\text{C}_6\text{H}_6\text{O}_5$, is produced, fusible at 116–117°, which still requires examination; it is not pyrotartaric acid. **Neutral Parapyruvates.**—The barium salt, $\text{C}_6\text{H}_6\text{O}_6\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$, is obtained by neutralising CO_3Ba by means of a solution of pyruvic acid (distilled at 63–66° under 30 m.m.), then adding a little CNK or KOH. A granular mass is formed, becoming anhydrous at 115°; it is then very hygroscopic. It is slightly soluble in water, easily so in acetate of soda and hydrochloric acid. Digested with acetic acid it takes a chalky appearance, and in that state contains $4\frac{1}{2}\text{H}_2\text{O}$ ($3\frac{1}{2}\text{H}_2\text{O}$ is given off in vacuo, the remainder at 120°). The calcium salt ($+4\text{H}_2\text{O}$), is similar to the barium salt, but more soluble. The lead salt is obtained by the addition of acetate of lead to a solution of pyruvic acid; the pyruvate of lead is not known, the acetate acting as a

condensation agent. The salt of zinc is obtained in the same manner in the form of small plates or a granular powder. The acid set at liberty from the barium salt is a colourless syrup which, according to analysis, is a mixture of 20 per cent of parapyruvic acid, and 80 per cent of lactonic acid, $\text{C}_6\text{H}_6\text{O}_5$. When we endeavour to transform parapyruvic acid entirely into its lactone by heating to 70°, it is split up into CO_2 and methylidihydrotrimesic acid. Concentrated soda produces the same reaction. Neutralised by alkalis the mixture of acid gives a parapyruvate; with carbonates in the cold we obtain lactonates; it is in this manner that the salt of barium is obtained ($\text{C}_6\text{H}_6\text{O}_5$) $_2\text{Ba}$, which is very soluble and precipitated by alcohol in colourless flakes; its aqueous solution is slightly acid, but gradually, especially when warmed, the parapyruvate is deposited, and the solution becomes very acid. The acid set at liberty from the lead salt by SH_2 is distinguished from that formed by the barium salt, in that it is transformed into a crystalline compound which gives phenylhydrazone fusible at 200°.—*Liebig's Annalen. Chem.*, cccv., p. 154.

On the Constitution of Tartarazine.—R. Anschütz.—Tartarazine is split up by reduction into soda salts of sulphanilic acid, and aminotartarazinogenic acid, $\text{C}_{10}\text{H}_8\text{N}_3\text{SO}_3\text{H}$:—



Monosodic aminotartarazinogenate, $\text{C}_{10}\text{H}_8\text{N}_3\text{SO}_3\text{Na}$, is obtained by heating a solution of 80 grms. of tartarazine and 40 grms. of NaCl in 800 c.c. of water, with 100 grms. of powdered zinc, until decolouration occurs, and then pouring the solution, which takes a violet colour when exposed to air, into 300 c.c. of concentrated HCl. Colourless needles, which are a mixture of the two acids, are precipitated. This mixture, weighing 30 grms. is dissolved in 200 c.c. of water, with the addition of 10·6 grms. of dry CO_3Na_2 . On the addition of 5 c.c. of HCl at 33 per cent, the soda salt in question, is precipitated in small colourless crystals. The free acid, $\text{C}_{10}\text{H}_8\text{N}_3\text{SO}_3\text{H}$ (sulphoxyphenyl-4-amidopyrazolone-3-carbonic acid), crystallises in dilute HCl in small slightly coloured heavy needles, almost insoluble in water, alcohol, and acetic acid, and slightly soluble in warm aqueous alcohol and warm HCl. Its solution in alkaline carbonates takes a violet colour on contact with the air. When heated it decomposes without melting.—*Liebig's Ann. Chem.*, cccvi., p. 1.

The Action of Semi-carbazide on Oxide of Mesityl.—C. Harries and F. Kaiser.—Two semi-carbazones from oxide of mesityl are described; the one prepared by the usual methods melts at 156°; submitted to distillation it changes into its isomer, fusible at 129°. The first only is split up by acids into semicarbazide and oxide of mesityl. The second is obtained by leaving equimolecular aqueous solutions of chlorhydrate of semicarbazide and oxide of mesityl in contact, in the cold, for twelve hours. The result of the reaction is a solid basic body, fusible at 130–131°, and apparently having the formula of a pyrazolic derivative, and not that of a semi-carbazone. The corresponding picrate crystallises in long yellow needles, fusible at 136–137°, slightly soluble in cold organic solvents.—*Berichte*, xxxii., p. 1338.

Preparation of Adipic Acid.—O. Aschan.—Adipic acid has already been prepared by the oxidation of a carbide boiling at about 80° , obtained from petroleum from Baku. The author uses this reaction as the basis of the preparation of adipic acid. That portion of the petroleum ether boiling at $78-82^{\circ}$ ($d=0.752$ at 15°) is utilised; it is heated in a retort fitted with a reflux condenser, with 10 parts of NO_3H ($d=1.42$). At the end of fifty or sixty hours, it is concentrated to one-quarter by distillation, then evaporated on a water-bath. The crystalline mass remaining is taken up with its own volume of cold water, and drained after twelve hours. It is then dissolved in NH_3 at 25 per cent, exhausted with ether, brought to boiling, and the acid precipitated by HCl . It is purified by crystallisation in boiling water, and fuses at 149.5° . 250 grms. of carbide give 44 grms. of adipic acid.—*Berichte*, xxxii, p. 1709.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Society of Arts, 8. (Cantor Lectures). "Photography of Colour," by E. Sanger Shepherd.
 — Royal Institution, 5. General Monthly Meeting.
 — Society of Chemical Industry, 8. "The presence of Naphthalene in Coal-gas," by R. W. Allen. "Notes on the Determination of the Iodine Value of Oils," by Arthur Marshall, A.I.C., F.C.S.
 TUESDAY, 6th.—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
 WEDNESDAY, 7th.—Society of Arts, 8. "Macombe's Country (South of the Zambesi), its Ancient Goldfields and Industrial Resources," by Dr. Carl Peters.
 — Society of Public Analysts, 8. "The Determination of Carbon and Sulphur in Steel," by Bertram Biount, F.I.C. "Maize Oil," by Rowland Williams, F.I.C. "Note on the Assay of Cresote," by A. D. Hall, M.A. "Note on the Influence of Temperature and Concentration on the Saline Constituents of Boiler Waters," by Cecil H. Cribb, B.Sc., &c.
 THURSDAY, 8th.—Royal Institution, 3. "Recent Excavations at the Argive Heraeum (in Greece)," by Charles Waldstein, Litt D., Ph.D., L.H.D.
 FRIDAY, 9th.—Royal Institution, 9. "Bacteria and Sewage," by Frank Clowes, D.Sc., F.C.S.
 SATURDAY, 10th.—Royal Institution, 3. "Polarised Light," by The Rt. Hon. Lord Rayleigh, M.A., D.C.L., &c.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2102.

THE ANALYSIS OF CAYENNE PEPPER.

By WILLIAM C. R. KYNASTON.

HAVING recently had occasion to examine some samples of Cayenne pepper, and not being able to find any recent work upon the subject, I have examined three samples of pepper of known purity with the following results:—

	A. Per cent.	B. Per cent.	C. Per cent.
Moisture.. .. .	9.90	8.90	9.12
Ethereal extract	21.08	20.91	20.97
Alcoholic extract	9.54	10.43	15.12
Woody fibre	22.09	25.30	17.96
Total ash	6.27	6.50	5.66
Insoluble ash.. .. .	1.22	1.51	1.10
Sand	0.11	0.06	0.16
Alkalinity of ash as K ₂ O ..	1.79	1.91	1.53
Percentage of alkalinity as K ₂ O in total ash ..	28.55	29.38	27.03

Sample marked A was ground in the laboratory from chillies.

Sample marked B was ground in the laboratory from Japan chillies.

Sample marked C was a sample of Cayenne pepper of known purity, as placed on the market.

The method of analysis was as follows:—

Moisture.—This item was the total loss at 100° C.

Ethereal Extract.—This was made by placing the dried sample in a dried filter-paper and extracting with ether, in a Soxhlet's apparatus, for a period of three hours.

Alcoholic Extract.—The residue from the ether extraction was completely extracted with hot alcohol.

Woody Fibre.—The residue from the alcoholic extraction was treated in the usual way for woody fibre.

The conclusions to be drawn from the above figures are:—

1. The ethereal extract seems to be practically constant.
2. The alkalinity of the ash seems to be practically constant.
3. The percentage of alkalinity to that of ash is fairly constant.

The Laboratory, 28, Chapel Street,
Liverpool.

THE CHEMICAL EXAMINATION OF HOPS AND OF EXTRACTS OF HOPS.

By ERNST HANTKE.

THE analysis of hops and of extracts of hops comprises the following determinations:—The water, the matter soluble in petroleum ether, the wax, the matter soluble in sulphuric ether, the tannin, and the ash.

The estimation of the water is effected by drying the hops at 100—102° until the weight is constant; this requires eight hours. Extract of hops is intimately mixed with calcined sand and carefully heated to 100—102°; this operation requires about twenty-four hours, the whole mass becomes hard.

For estimating the matters soluble in petroleum ether, the hops are first kept at 50° for two days, after which they are further dried in the exsiccator for two days. Extract of hops is first mixed with calcined sand. The

extraction is carried out in a Soxhlet extractor, and the petroleum ether used should boil at a temperature lower than 50°. Its density would then be from 0.6616 to 0.6620 at 15°. The extraction is complete after eight or nine hours. The petroleum ether is driven off on the water-bath and the residue dried. When it is necessary to estimate the soft resin in the matter soluble in petroleum ether, the residue is treated with alcohol at 90 per cent (by volume) at the ordinary temperature, shaking occasionally until complete solution is effected. This operation requires nearly a day. The colour of the solution gives certain indications as to the place of origin of the hops.

The alcoholic solution is filtered into a small tared flask, the residue well washed with alcohol, which latter is driven off by heat. The residue which consists of the pure soft resin is weighed.

The difference between the soft resin and the matter soluble in petroleum ether gives the wax.

The hard resin is determined by submitting the hops, already treated with petroleum ether, to the solvent action of anhydrous sulphuric ether ($d=0.7283$ at 15°). The extraction by ether proceeds fairly rapidly, and is generally complete after the lapse of three hours. The ether is then driven off and the residue weighed.

To estimate the tannin, 6 grms. of hops, or of extract, are boiled for five hours with 400 c.c. of water in a flask fitted with a vertical condenser; fill up to 500 c.c. and filter. 100 c.c. of the clear solution are taken and evaporated to dryness; this gives the soluble matter. The remainder of the filtrate is submitted to the action of a skin filter, and 100 c.c. of the solution containing the non-tanning material are evaporated down. The difference between the results obtained in the first place, and the residue obtained after the absorption of the tanning material enables us to estimate the quantity of tannin present.

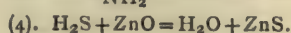
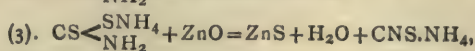
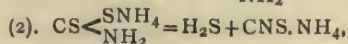
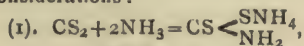
The ash is determined in the usual manner.

The results of a large number of analyses shows that a pound of extract of hops is equal to 12 pounds of hops, a fact which is confirmed in practice.—*Chemiker Zeitung*, 1899, p. 545.

THE ESTIMATION OF BISULPHIDE OF CARBON.

By Dr. A. GOLDBERG.

THE method of estimating bisulphide of carbon which I am about to describe is based on the following theoretical considerations:—



The different reactions take place in part successively, and in part simultaneously, but finally the quantity of zinc sulphide formed is equivalent to the quantity of sulphide of carbon which entered into the reaction, so that the calculation can be easily made according to the simple relation $\text{CS}_2 = \text{H}_2\text{S} = \text{Zn}$.

The reagents required are:—An ammoniacal solution of zinc of known strength, and a solution of sodic sulphide titrated by means of the zinc solution. The substance under examination is heated on a water-bath with alcoholic ammonia to a temperature of about 60°, but a temperature of 100° does no harm; the operation is carried out in a small flask stout enough to bear pressure, and the stopper should be firmly held in. Into this flask is poured 1 grm. of the sample of sulphide of carbon, 5 or 6 c.c. of ammonia ($d=0.970$), and about 25 c.c. of absolute alcohol;

it is then tightly closed and left to stand in a warm place. When the reaction is finished, the solution should be of a yellow colour; the contents of the flask are poured into a beaker and considerably diluted, a known volume of the ammoniacal solution of zinc is then added, and the whole heated to boiling with continuous stirring, and the excess of zinc determined by the aid of a titrated solution of sodic sulphide in the presence of nitro-prussiate of soda as an indicator.

When more than 0.2 grm. of bisulphide of carbon is taken for estimation, it is better to make up to a known volume, and then take an aliquot part for the titration.

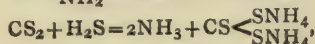
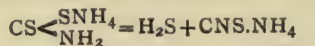
The following are the results of a few estimations, made according to the method just described, on samples of perfectly pure bisulphide of carbon:—

Grm.	Grm.	Grm.	Per cent.
0.2178 CS ₂ used	0.1861 Zn	= 0.2175 CS ₂	= 91.86
0.4723 " "	0.4041 " "	= 0.4725 " "	= 100.05
0.4502 " "	0.2843 " "	= 0.4494 " "	= 99.82

It has been mentioned above that the solution has a yellow colour after heating; at the ordinary temperature, it is of a reddish yellow colour from the commencement. When diluted, after some hours, with a large quantity of water, it gives a perfect solution, but it absorbs a slightly smaller quantity of zinc. In this manner, a known quantity of bisulphide of carbon has given the following results:—

1. *Hot*.—(a) 0.2190 grm. Zn; (b) 0.2175 grm. Zn; (c) 0.2181 grm. Zn; (d) 0.2175 grm. Zn; (e) 0.2181 grm. Zn. Mean, 0.2180 grm. Zn = 0.2549 grm. CS₂ = 100.27 per cent.
2. *At the Ordinary Temperature*.—(a) 0.2123; (b) 0.2116; (c) 0.2116; (d) 0.2135; (e) 0.2116; (f) 0.2117 grm. Zn. Mean 0.2122 = 97.6 per cent of the theoretical amount.

This is probably due to the formation of a certain quantity of sulphocarbonate of ammonia at the ordinary temperature:—



a body which gives, during titration, ZnCS₃, which, on boiling, is mostly transformed into ZnS and CS₂. The result is that, with this secondary reaction taking place at the ordinary temperature, the relation is no longer Zn = H₂S = CS₂, but Zn = 2H₂S = 2CS₂.

The reaction is not changed if, instead of using alcoholic ammonia, ordinary aqueous ammonia be taken, but a longer time is necessary to complete the reaction. For example, 5 c.c. of bisulphite of carbon were treated with 30 c.c. of aqueous ammonia of 0.91 density, and heated for some days until the bisulphide of carbon had completely disappeared.

The solution, cooled to the surrounding temperature, was diluted to 250 c.c.; 10 c.c. required 0.2176 grm. of Zn (instead of 0.2174); that is, 100.09 per cent found.—*Zeitschrift für Angewandte Chemie*, 1899, p. 75.

The Preparation of Fuming Nitric Acid.—L. Vaning.—When we add concentrated nitric acid to formic aldehyde in solution, the liquid, in the cold, takes a yellow colour, and gives off abundant fumes of binoxide of nitrogen. This reaction can be utilised for the preparation of fuming nitric acid. In fact, if we react with polymerised formic aldehyde on nitric acid, fumes of binoxide of nitrogen are given off in the cold, but on moderately heating hyponitric acid is given off, which passed into nitric acid gives a product rich in binoxide of nitrogen. We can obtain an acid rich in nitrous fumes without distillation by gradually adding polymerised formic aldehyde.—*Berichte*, xxxii., p. 1392.

ON THE ABSORPTION OF IODINE BY PLANTS.

By P. BOURCET.

DIFFERENT plants grown in the same soil absorb the various mineral substances contained by the soil in different proportions. Bunsen long ago observed that certain kinds of plants had the power of removing rubidium from soils in which this metal was present in such small quantities that it could not be detected even by spectrum analysis. Grandaue made similar observations with lithium and caesium. It occurred to me that certain plants ought to absorb the iodine necessary to their structure and protoplasm from the soil or from water, and perhaps with the accompaniment of special functions. But as experiments on a large number of species would have taken me too far, I have limited these first experiments to a certain number of edible plants, my intention being to study at the same time how the iodine was introduced by alimentation into the animal economy.

Several cubic metres of earth were well broken up and made thoroughly homogeneous by several successive siftings. Five samples taken at hazard in the mass were found to contain an average of 0.83 m.grm. of iodine per 100 kilograms of soil. This earth was spread out, and a certain number of seeds were sown in it. The crops were gathered as they reached maturity, and the iodine they contained was estimated by the method already described (*Comptes Rendus*, vol. cxviii., p. 1120; *Bull. Soc. Chim.*, Series 3, vol. xxi., p. 554). The following are the results obtained:—

	M.grm. of iodine per kilo.
Solanaceae—	
<i>Solanum tuberosum</i> (potato)	0.000
<i>Lycopersicum esculentum</i> (tomato)	0.07
<i>Solanum melongena</i> (egg plant)	0.01
Cucurbitaceae—	
<i>Cucumis sativus</i> (cucumber)	0.012
" " (gherkin)	0.00
" " melo (melon)	0.06
<i>Cucurbita maxima</i> (pumpkin)	0.017
Cruciferae—	
<i>Raphanus sativus</i> (radish)	0.18
<i>Brassica napus</i> (turnip)	0.24
" " (long radish)	0.16
<i>Raphanus</i> " (black radish)	0.00
Chenopodeae—	
<i>Beta rapa</i> (beetroot)	0.14
" " cycla (skin of beetroot)	0.38
<i>Spinacia oleracea</i> (spinach)	0.021
Leguminosae—	
<i>Faba vulgaris</i> (bean)	0.14
<i>Phaseolus vulgaris</i> (French beans)	0.32
" " (kidney beans)	0.013
<i>Pisum sativum</i> (green peas)	0.084
Liliaceae—	
<i>Allium sativum</i> (garlic)	0.94
" " cepa (onions)	0.24
" " porrum (leeks)	0.12
Polygonaeae—	
<i>Rumex acetosa</i> (sorrel)	0.047
Umbelliferae—	
<i>Scandix cerfolium</i> (cherville)	0.14
<i>Petroselinum sativum</i> (parsley)	0.00
<i>Daucus carotta</i> (carrot)	0.00
Synanthereae—	
<i>Lactuca sativa</i> (lettuce)	0.096
<i>Cichorium intybus</i> (chicory)	0.000
" " <i>angustifolium</i> (endive)	0.000

This table shows that under identical conditions of soil, moisture, and exposure some plants absorb much more iodine than others, and that some, on the other hand, do not absorb a trace.

Unfortunately, my experiments were carried out on too restricted a number of plants for me to be able to definitely observe the numerous conditions which affect this absorption. They have, however, been sufficient to show that certain families, the *Liliaceae* and the *Chenopodeae*, accumulate much more iodine than certain others, such as the *Solaneae* or the *Umbelliferae*, for example. We also see that, in the same vegetable family, the absorption of this metalloid varies with each variety; the *Synantheraea* and the *Cruciferae* give very decided examples.

In a forthcoming paper I propose showing that this phenomenon of specific selection of iodine also takes place in the various organs of the same animal species.—*Bull. Soc. Chim.*, Series 3, xliii., No. 1.

A NEW METHOD OF METHYLATION.

By MAURICE PRUD'HOMME.

THIS method depends on the combined action of formic aldehyde and nascent hydrogen in an acid medium. By its means I have been able, by methylation, to transform a certain number of colouring materials and leuco bases, containing groups of NH_2 . The equation of the reaction is written, $\text{RNH}_2 + \text{CH}_2\text{O} + \text{H}_2 = \text{RNHCH}_3 + \text{H}_2\text{O}$.

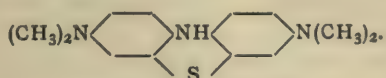
Transformation of Fuchsin into Hexamethylated Violet.—A solution of fuchsin, to which is added hydrochloric acid, zinc powder, and formic aldehyde, is gently heated to $75-80^\circ$ for about a quarter of an hour. The colourless liquid is filtered, cooled, and oxidised in the presence of acetic acid, with 1 molecule of PbO_2 per 1 molecule of fuchsin. The lead is removed by means of SO_4Na_2 , and the colouring matter precipitated by NaCl .

Cotton, mordanted with tannin and tartar emetic, takes a violet colour, only different to hexamethylated violet (hexamethyl parafuchsin) by its slightly bluish tint, which is probably due to the fact that commercial fuchsin is not pure β -fuchsin, but a mixture of fuchsins of C_{19} and C_{20} .

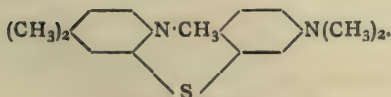
Rhodamine of m-Aminophenol into Methylated Rhodamine.—The rhodamine of m-aminophenol colours wool, mordanted with tannin, orange. When treated with formic aldehyde, zinc, and hydrochloric acid it becomes methylated. Filtered, the colourless solution gradually regains its colour on exposure to the air. The new rhodamine gives wool, silk, and cotton, mordanted with tannin, the beautiful red shades, of the special tone belonging to the colouring matters of this class.

Thionine into Methylene Blue.—Methylene blue represents tetramethylated thionine (*Lauth violet*). The transformation under the conditions already described is easily effected. Dyed materials, subjected to several successive treatments, re-oxidised in the air, lead to the identification of a new colouring material with methylene blue. When the action of the reagents is pushed further we obtain a second colouring material which dyes cotton treated with tannin and tartar emetic a much greener blue than methylene blue.

It is probable that the methylation, after having acted on the aminogene groups, also takes place with the inside group, NH , of the leuco-base of methylene blue.



Leuco-base of methylene blue.



Methylated leuco-base.

According to Bernthsen, this latter becomes oxidised, giving a blue closely resembling methylene blue, but furnishing a dye of different shades.

Methylene blue, treated directly with CH_2O , Zn , and HCl , gives the same greenish blue colouring materials.

Transformation of Safranines.—We heat a solution of phenosafranine at 1 grm. per litre, in the presence of Zn and HCl , to about $75-80^\circ$, until the reduction and decolouration is complete. At this moment the addition of CH_2O instantaneously re-colours the solution a violet-red. A part of this solution, filtered and precipitated by NaCl , will dye cotton mordanted with tannin. The tint is similar to that of Witt's neutral red. If the reaction is prolonged for several minutes the violet-red changes to violet. Finally, after the reaction has lasted about half an hour the colourless, filtered liquid gradually becomes re-oxidised, and takes a blue colour. The colouring material, precipitated by means of NaCl , gives cotton, treated with tannin and emetic, wool, and silk a violet-blue colour.

This blue colour may be an *induline*. It dissolves with an olive colour in SO_4H_2 , which becomes a bluish grey on dilution. Generally the safranines give, with SO_4H_2 , a green solution, rendered first blue, and then violet by dilution.

Possibly, besides the methylation of the aminogene groups, there may be one produced in the nitrogen of the azonium, by substitution of the hydrogen of the fixed leuco derivative by nitrogen. We have seen above that CH_2O acts as an oxidising agent on the N or the H of the leuco derivative of safranine.—*Moniteur Scientifique*, Feb., 1900, Series 4, xiv.

ON THE ELECTROLYTIC PREPARATION OF PERCHLORIC ACID AND OF ITS SALTS.

By F. FORSTER.

THE author has already shown (*Zeit. für Elek.*, ii., p. 270) that when a basic solution of an alkaline iodate is electrolysed a reduction takes place at the anode. This does not occur in the case of the chlorates; that is, if we use a cathode of platinum, lead, copper, zinc, or nickel. By using an iron or cobalt cathode, however, the chlorates can be electrolytically reduced to chlorides. We propose here to deal only with electrolysis in neutral or acid solution; in this case the chlorate is peroxidised into perchlorate—a fact already observed by Stadion and Kolbe.

To examine the influence of various external conditions on the oxidation, we electrolysed 100 c.c. of a solution of known strength between two platinum electrodes of 12 square c.m. surface; the whole being placed in a glass cylinder, hermetically sealed, through the cork of which passed, besides the wires, a glass tube for carrying off any gas disengaged. The gas given off was analysed, as was also that given off concurrently from a gas voltmeter placed in the circuit. According to the proportion of oxygen present in the two gases, the percentage of current used for oxidation was calculated. The returns, expressed in percentages of the theoretical amount obtained under various conditions, are given in the accompanying table. The current densities are expressed in amperes per square decimetre.

The solutions of chlorate of potassium and sodium used were neutral; the first contained a little sea-salt, which was transformed into chlorate then perchlorate, without interfering with the phenomenon. The degrees of concentration were chosen in such a way that the solutions of chlorate of soda should be either equivalent to, or four times greater than, that of chlorate of potassium at 5 per cent. The solution of chloric acid was nearly twice that of the chlorate. After electrolysis for a short while, the slightly soluble perchlorate is precipitated from the solu-

Temperature..	17-20°.								75°.				
Current Density ..	16.6.		8.3.		4.1.		0.83.		16.6.	8.3.			
Duration of experiment ..	5'. 3 hr.		10'. 1½ hrs.		20'. 3 hrs.		2 hrs. 4 hrs.		5'. 3 hr.	10'.			
Returns with a	{	5 per cent KClO ₃ ..	75	64	64	65	—	—	33	43	—	—	0.0
solution of .		4.2 per cent NaClO ₃ ..	75	69	63.5	63.5	63	56	—	—	—	—	—
		17 per cent NaClO ₃ ..	89	90	83	88	67	83	50	46	13	8	—
		6.5 per cent HClO ₃ ..	—	—	79	87	—	—	—	—	—	—	—

tion of chlorate of potash at the anode. This salt can also be prepared by adding chloride of potassium to a solution of perchlorate of soda or perchloric acid. The salt thus obtained with perchloric acid loses 45.9 per cent of its weight at a red heat; the salt KClO₄ should lose 46.2 per cent.

The table shows that, for currents of too low densities, the return increases with the concentration. From the fact of the feeble solubility of chlorate of potash at a low temperature, and also that in this case we cannot use warm solutions, it is preferable to use chlorate of soda for preparing the perchlorates.

The following are the results obtained with a 50 per cent solution of NaClO₃ at the ordinary temperature with a current density of 8.3 ampères per square decimetre; the tension being 4.5 volts at the electrodes when these are 1.5 c.m. apart.

Time from the commencement.	Return, per cent of theory.
10 minutes..	86*
5 hours ..	95
20 " ..	98
24½ " ..	95
27½ " ..	24
29½ " ..	28

* In another experiment we obtained 95 per cent after ten minutes.

To transform 50 grms. of chlorate of soda into perchlorate requires twenty-five hours theoretically with the current used above, viz., 1 ampère. It can be seen that the useful effect of the current and the proportion of chlorate transformed are very considerable. By doubling the current no other result was noticed beyond diminishing the duration of the experiment by half and an increase of electromotive force to 5.2 volts. Towards the end of the experiment the smell of ozone became more and more pronounced.

The solutions of perchlorate obtained by the preceding experiments were treated with the theoretical amount of KCl. We thus obtained in KClO₃ 78-85 per cent of the quantity of NaClO₃ in solution. The salt obtained retained a small proportion of chlorate. By simply measuring the oxygen given off, we obtained 45.7 and 45.5 per cent, instead of 46.2 per cent which should be given off by the pure salt.

With solutions of KClO₃ the results, as we have seen, are not so good. An experiment was made with three litres of a 5.6 per cent solution of the salt, using a platinum anode between two nickel cathodes. In this manner we obtained 82 per cent of the theoretical return, estimated by means of a copper voltameter placed in the circuit; but, when once about half the chlorate was oxidised, the return decreased with great rapidity. The production of perchlorate thus takes place as well in an acid as in a neutral solution. In alkaline solution we have only observed an energetic oxidation at the commencement, which is the stronger as the strength of the current is greater, but which decreases after a certain time. The following series of observations, made on a 50 per cent solution of NaClO₃, containing 1 per cent of NaHO, with a current strength of 1 ampère (equal to 8.3 ampères per square decimetre) shows this fact plainly:—

The quantities of oxygen used at the anode were, in percentages of the oxygen produced by the current—

After 1 minute ..	20 per cent
" 3 hours ..	8 "

The strength of the current was then increased to 2.3 ampères (equal to 23.3 ampères per square decimetre), and the results obtained were:—

After 10 minutes ..	54 per cent
" 30 " ..	53 "
" 1½ hours ..	44 "
" 4 " ..	2 "

It does not therefore seem possible, according to our experiments, to obtain perchlorates directly from the electrolysis of chlorides, as the intermediate product—the chlorate—can only be formed in alkaline solution; the alkali being produced by the current.—*Zeitschrift für Elektrochemie*, iv., p. 373.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

THIRD PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE AND OXIDE.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

THE two preceding papers (*Proc. Amer. Acad. of Arts and Sciences*, 1897, xxxiii., 113, and 1898, xxxiv., 351; *CHEMICAL NEWS*, lxxvii., p. 20, and lxxix., p. 199), describing the earlier part of this investigation, were concerned with the complete analysis of cobaltous bromide. Both the cobalt and the bromine in this compound, as well as the trace of inevitable impurity, were determined with care, and the consistent verdict of all the results pointed toward a value between 58.99 and 59.00 for the number sought. The danger of the existence of an unknown error in a result thus obtained from a single compound is too well known to need emphasis; and with this danger in mind we sought to obtain support from wholly different data. The present paper describes two series of determinations, which, while less satisfactory than the work with the bromide, are nevertheless of corroborative value, and moreover serve to point out some of the pitfalls which ensnared the earlier experimenters.

I. The Reduction of Cobaltous Chloride.

Cobaltous chloride was chosen first as the basis of the confirmatory work, both on account of the ease with which it can be prepared and because it can be heated to a much higher temperature than the bromide without danger of vaporisation. These circumstances allow greater surety both in drying and in reducing.

Owing to the comparatively slight volatility of cobaltous chloride, and to the difficulty of obtaining chlorine in a sufficiently pure state, we made no attempt to purify the salt by sublimation. The preparation of cobaltous chloride in aqueous solution was inadmissible on account of the certain presence of oxide in the dried and ignited substance under these conditions; hence the method finally adopted was the ignition of carefully purified purpureo-cobaltic chloride, which may be dried before it decomposes.

A considerable quantity of this compound was prepared by passing air through a strongly ammoniacal solution of

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxv., No. 3, 1899.

cobaltous chloride, and subsequently acidifying the mixture with hydrochloric acid. The precipitate was then re-crystallised six times by solution in pure re-distilled ammonia in a platinum dish and precipitation with re-distilled hydrochloric acid in a Jena glass flask. This latter operation could not be performed in platinum, because of the liberation of small quantities of chlorine. The final precipitate was collected on a pure washed filter and dried. In order to convert the amine into cobaltous chloride it was heated in an air-bath to about 200°, until it was entirely decomposed without fusing. Owing to the fact that the dried salt melts at a temperature very slightly above that at which it breaks up, the heat was applied very gradually. Here again the liberation of traces of chlorine prevented the use of platinum, a porcelain crucible being used to contain the salt. The corresponding purpureo-bromide of cobalt melts at a temperature too near its decomposing-point to have allowed the use of a similar method for preparing cobaltous bromide in the earlier part of this research.

The cobaltous chloride thus prepared, still containing a large amount of ammoniac chloride, was now heated in the platinum boat in a rapid current of dry nitrogen and hydrochloric acid gas until ammoniac chloride ceased to be expelled. The drying apparatus used in the work upon the bromide was re-filled, and easily altered for this purpose by substituting a strong solution of hydrochloric acid for the bromine and red phosphorus. The hydrochloric acid gas was displaced by pure nitrogen, and this in turn by pure air; and finally the dry cobaltous chloride was transferred to the weighing bottle by means of the usual bottling apparatus.

After having been weighed, the chloride was reduced in hydrogen in the manner already described under the analysis of cobaltous bromide.

During the reduction no trace of cobaltous chloride sublimed from the boat, but a slight sublimate of ammoniac chloride appeared in the tube. The amount of this sublimate was determined by washing out the tube with pure water and Nesslerising the solution, and this amount was subtracted from the original weight of cobaltous chloride. Probably the correction was somewhat too great, for traces of ammoniac bromide appeared in every reduction of cobaltous bromide, when no ammonia could have been present in the salt; but the error arising from this source must have been small.

A small quantity of alkaline chloride was found in the residual cobalt, and was determined in the usual way by lixiviating the metal and evaporating the solution. This correction was of course subtracted from the original weight of the cobaltous chloride, as well as from that of the metal.

In the following table of results the specific gravity of cobaltous chloride is assumed to be 2.94, the value given by Joule and Playfair (Landolt and Börnstein, *Tabellen*, 1894, p. 134). This necessitates a correction to the vacuum standard of +0.000262 gm. per gm. of chloride. Cobalt itself has a specific gravity too near that of brass to need any correction of this kind. Cl=35.455.

Observed weight of cobaltous chloride		
in vacuum	4.16702	2.30588
Observed weight of cobalt in vacuum ..	1.89304	1.04771
Weight of residue	0.00061	0.00048
Weight of ammoniac chloride	0.00158	0.00028
Corrected weight of cobaltous chloride ..	4.16483	2.30512
Corrected weight of cobalt	1.89243	1.04723
Atomic weight of cobalt	59.053	59.035
Average	59.044	

As the alkali had not been completely removed by the process of crystallisation to which the cobaltamine had been subjected, it is highly probable that some silica also remained which was not removed from the metal by leaching. This probability, together with the fact that the ammoniac chloride correction is undoubtedly somewhat

too large, seems sufficient to account for the fact that these results are slightly higher than those obtained in the bromide series (58.995). At any rate the evidence of this method is that the atomic weight of cobalt cannot be greater than 59.05, for none of the probable errors would tend to make this result too low.

(To be continued).

A TABLE OF ATOMIC WEIGHTS

OF SEVENTY-FOUR ELEMENTS.*

By THEODORE WILLIAM RICHARDS.

Name.	Symbol.	Atomic weight.
Aluminium ..	Al	27.1
Antimony ..	Sb	120.0
Argon ..	A	39.9?
Arsenic ..	As	75.0
Barium ..	Ba	137.43
Beryllium ..	Be=Gl	9.1
Bismuth ..	Bi	208.0
Boron ..	B	10.95
Bromine ..	Br	79.955
Cadmium ..	Cd	112.3
Cæsium ..	Cs	132.9
Calcium ..	Ca	40.1
Carbon ..	C	12.001
Cerium ..	Ce	140.0
Chlorine ..	Cl	35.455
Chromium ..	Cr	52.14
Cobalt ..	Co	59.00
Columbium ..	Cb=Nb	94.0
Copper ..	Cu	63.60
"Didymium" ..	Nd+Pr	142 ±
Erbium ..	Er	166.0
Fluorine ..	F	19.05
Gadolinium?	Gd	156.0?
Gallium ..	Ga	70.0
Germanium ..	Ge	72.5
Glucinum ..	Gl=Be	9.1
Gold ..	Au	197.3
Helium ..	He	4.0?
Hydrogen ..	H	1.0075
Indium ..	In	114.0
Iodine ..	I	126.85
Iridium ..	Ir	193.0
Iron ..	Fe	56.0
Lanthanum ..	La	138.5
Lead ..	Pb	206.92
Lithium ..	Li	7.03
Magnesium ..	Mg	24.36
Manganese ..	Mn	55.02
Mercury ..	Hg	200.0
Molybdenum ..	Mo	96.0
Neodymium ..	Nd	143.6
Nickel ..	Ni	58.70
Niobium ..	Nb=Cb	94.0
Nitrogen ..	N	14.045
Osmium ..	Os	190.8
Oxygen (standard) ..	O	16.000
Palladium ..	Pd	106.5
Phosphorus ..	P	31.0
Platinum ..	Pt	195.2
Potassium ..	K	39.140
Praseodymium ..	Pr	140.5
Rhodium ..	Rh	103.0
Rubidium ..	Rb	85.44
Ruthenium ..	Ru	101.7
Samarium? ..	Sm	150.0
Scandium ..	Sc	44.0
Selenium ..	Se	79.2

* Compiled in April, 1899, from the most recent data.

Name.	Symbol.	Atomic weight.
Silicon ..	Si	28.4
Silver ..	Ag	107.930
Sodium ..	Na	23.050
Strontium ..	Sr	87.68
Sulphur ..	S	32.065
Tantalum ..	Ta	183.0
Tellurium ..	Te	127.5?
Terbium? ..	Tb	160.0
Thallium ..	Tl	204.15
Thorium ..	Th	233.0
Thulium? ..	Tu	170.0?
Tin ..	Sn	119.0
Titanium ..	Ti	48.17
Tungsten ..	W	184.4
Uranium ..	U	240.0
Vanadium ..	V	51.4
Ytterbium ..	Yb	173.0
Yttrium ..	Yt	89.0
Zinc ..	Zn	65.40
Zirconium ..	Zr	90.5

NOTE.

Since the appearance of this table in 1898, the Committee of the German Chemical Society (Messrs. Landolt, Ostwald, and Seubert) have made their interesting report upon the subject, and have invited the chemists of the world to join them in deciding upon one standard to be used everywhere. The fulfilment of this very desirable end must necessarily be a matter of many months; hence the present table is re-published this year in accordance with the original plan. It is to be distinctly understood that the re-publication is not in any way an attempt to compete with or to forestall the International Committee; it is merely an expression of opinion, which may be of temporary service. The fact that none of the other recent tables follow the accepted scientific usage concerning significant figures seems to afford an additional reason for reprinting this one.

The investigations of the past year have pointed to a change in four values given in the table of 1898. Calcium is made 40.1, instead of 40; for recent experiments (as yet unpublished) in this laboratory indicate that last year's estimate was too low. Neo- and praseodymium were oddly transposed by their discoverer, and the more accurate values of Jones (*Am. Chem. Journ.*, 1898, xx., 345; *CHEMICAL NEWS*, lxxvii., 280) and others are substituted. Lastly, Denher's (*Journ. Am. Chem. Soc.*, 1898, xx., 555; compare Clarke, *Ibid.*, 1899, xxi., 200; *CHEMICAL NEWS*, lxxix., 195) careful investigation upon selenium seems to show that this element has a higher atomic weight than was formerly supposed to belong to it. For the present a compromise number, 79.2, is recorded above.—*Proceedings of the American Academy of Arts and Sciences.*

Royal Institution.—The Right Hon. Rayleigh, F.R.S., will not deliver the second of his course of Lectures on "Polarised Light" at the Royal Institution on Saturday afternoon next (the 10th inst.), owing to the sudden death of his mother, the Dowager Lady Rayleigh. There will be no Lecture on Saturday afternoon.

International Exhibition at Canea, 1900.—On the 11th April next there will be opened by Prince George of Greece, "The First International Exhibition at Canea," the capital of Crete. No effort will be spared by the Government to make it a success; the Austrian, Italian, Greek, and Russian steam navigation companies will endeavour to make the passage to Crete as convenient and frequent as possible, and it is considered that a profitable market can be opened up in the island for a variety of goods. All particulars as to cost of space, &c., can be obtained from Mr. Arthur Gobiet, Prague, Carolinenthal, Bohemia, Austria. The Exhibition will remain open until the 7th of May, 1900.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 15th, 1900.

Sir HENRY ROSCOE, LL.D., F.R.S., Vice-President, in the Chair.

(Concluded from p. 103).

*21. "The Combination of Sulphur Dioxide with Oxygen." By EDWARD JOHN RUSSELL and NORMAN SMITH.

The authors have found that when a mixture of sulphur dioxide and oxygen acts on certain oxides, in addition to the absorption of the sulphur dioxide, part of the sulphur dioxide and oxygen combine, forming sulphur trioxide, this being apparently due to the "surface action" of the oxide. The extent of this "surface action" varies with the nature and physical conditions of each oxide. No sulphur trioxide was ever found unless a simultaneous absorption of sulphur dioxide occurred; when manganese peroxide and sulphur dioxide, dried by phosphorus pentoxide, were brought together, no absorption took place, nor was any sulphur trioxide produced on the addition of dried oxygen.

If a mixture of dried sulphur dioxide and oxygen be passed over well-dried platinised pumice heated to 400–450°, very little sulphur trioxide is formed, and the drier the materials the less is the combination.

*22. "Notes on the Estimation of Gaseous Compounds of Sulphur." By EDWARD JOHN RUSSELL.

In this paper volumetric methods of analysis are given which have been found to work satisfactorily in the estimation of sulphur dioxide, hydrogen sulphide, carbonyl sulphide, and carbon disulphide in gaseous mixtures. It is found that, except in the case of sulphur dioxide, absorption methods are not reliable; as a rule, by far the most satisfactory method is to explode with oxygen. In this explosion, sulphur dioxide and sulphur trioxide are both produced, the amount of the former being determined directly, and that of the latter calculated from the contraction observed after explosion. Sulphur dioxide is best estimated by absorption with a pellet of lead peroxide, since this substance, if freshly washed and not too dry, exerts but little of the surface action which tends to cause some of the sulphur dioxide to combine with part of the oxygen to form sulphur trioxide.

*23. "The Influence of the 'Nascent State' on the Combination of Dry Carbon Monoxide and Oxygen." By EDWARD JOHN RUSSELL.

The author has studied several reactions in which carbon monoxide and excess of oxygen were brought together in the flame of an explosion, one or both being in the nascent condition. Combustion was rarely complete, and the amounts of carbon monoxide left unburnt were found to be very similar to those left unburnt in Dixon's experiments (*Trans.*, 1896, 784), in which dried mixtures of carbon monoxide and oxygen were fired by adding carbon disulphide and oxygen, and sparking, although in the present experiments one of the substances (carbon monoxide) was in the nascent condition, whilst in Dixon's experiments it was not. It seems, therefore, that the nascent condition has no great effect in promoting combination between carbon monoxide and oxygen, although the high temperature produced by a violent reaction has a very considerable effect.

The substances used as sources of nascent carbon monoxide were carbonyl sulphide and nickel carbonyl; and for nascent oxygen, chlorine monoxide and chlorine peroxide.

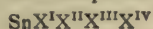
It was discovered incidentally that mixtures of pure carbonyl sulphide and excess of oxygen are not exploded by an electric spark. If, however, a slight amount only

of impurity is present, an explosion takes place, but combustion is not complete, carbonyl sulphide remaining unburnt in large quantity, along with carbon monoxide, produced by the decomposition of some of the carbonyl sulphide. If the impurity is greater, the combustion is complete.

*24. "Asymmetric Optically Active Tin Compounds. *Dextromethyl ethyl-n-propyl Tin Iodide*." (Preliminary Note). By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

Hitherto no substance containing an atom of tin attached to four different groups has been obtained, owing to the lack of general methods for their preparation.

The authors find that compounds of the type—

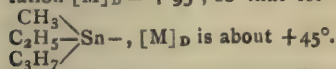


can be readily prepared by aid of the following series of reactions from the trimethyl tin iodide described by Ladenburg and Cahours:—

- (1). $2\text{Sn}(\text{CH}_3)_3\text{I} + \text{Zn}(\text{C}_2\text{H}_5)_2 = 2\text{Sn}(\text{CH}_3)_3(\text{C}_2\text{H}_5) + \text{ZnI}_2$.
- (2). $\text{Sn}(\text{CH}_3)_3(\text{C}_2\text{H}_5) + \text{I}_2 = \text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{I} + \text{CHI}_3$.
- (3). $2\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{I} + \text{Zn}(\text{C}_3\text{H}_7)_2 = 2\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7) + \text{ZnI}_2$.
- (4). $\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7) + \text{I}_2 = \text{Sn}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)\text{I} + \text{CHI}_3$.

Externally compensated *methylethyl-n-propyl tin iodide*, $\text{CH}_3 > \text{Sn} < \text{C}_3\text{H}_7$, the final product of reaction (4) is a faintly yellow oil boiling at 270° without decomposition; it is almost insoluble in water, and its vapour exercises unpleasant effects on the mucous membrane.

On agitating the iodide with a warm aqueous solution of a molecular proportion of silver dextrocamphorsulphonate, and evaporating the filtered liquid, a copious deposit of *dextromethylethyl-n-propyl tin dextrocamphorsulphonate*, $\text{Sn}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)(\text{C}_{10}\text{H}_{15}\text{OSO}_3)$, was obtained; the salt is only sparingly soluble in cold water, and crystallises in lustrous square plates melting at $125-126^\circ$. In dilute aqueous solution it has the molecular rotation $[\text{M}]_D = +95^\circ$, so that for the monobasic radicle,



On evaporating the mother-liquor from which this salt had separated, further deposits of the same salt were obtained until all the water had been expelled, and the authors have been unable to isolate a salt of the laevo-base; this behaviour seems due to the conversion of the laevo-base into the dextro-base by continued racemisation in the following manner:—The solution of externally compensated base with dextrocamphorsulphonic acid deposits a portion of its dextro-base as the sparingly soluble salt; the excess of laevo- over dextro-base remaining in the solution racemises as evaporation proceeds, a further portion of dextro-base separates as salt, and racemisation of the residue again proceeds. This case is the first of the kind recorded, and affords powerful support to Le Bel's hypothesis respecting the mobility of alkyl groups of low molecular weight in quaternary ammonium salts.

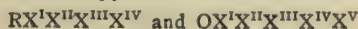
On treating the freshly prepared cold aqueous solution of the dextrocamphor sulphonate with potassium iodide solution, *dextromethylethyl-n-propyl tin iodide* separates as a faintly yellow oil; the highest specific rotation of the iodide which has yet been observed is $[\alpha]_D = +23^\circ$ in ethereal solution. The rotation was, however, very variable, and, under conditions not yet understood, the separated iodide was optically inactive. This behaviour is due to racemisation.

It should be noted that the discovery noted above, that racemisation, due to intramolecular mobility, may cause rapid and complete conversion of an externally compensated base into one optically active isomeride, reopens

the question of the space configuration of quadrivalent sulphur compounds which, in the light of previous knowledge, seemed to have been determined by our former results (*Proc.*, 1900, xvi., 12).

Having now shown that quadrivalent asymmetric tin compounds can exist in enantiomorphously related configurations possessing optical activity, it follows that the space configuration of quadrivalent tin compounds is of the tetrahedral type already established for carbon compounds, and substances of the type of tin tetrachloride must now be regarded as true atomic compounds. Having proved that asymmetric pentavalent nitrogen compounds (*Trans.*, 1899, lxxv., 1127) also give rise to optical activity in the same way that van't Hoff and Le Bel proved it for carbon, it may be concluded that all enantiomorphous compounds must be optically active.

In Group IV. of the periodic table the non-metal, carbon, is at the top, whilst the metal, tin, is near the bottom; since both can give rise to optical activity in their asymmetric compounds, it is highly probable that all the elements in Group IV. lying between these are capable of acting as centres of optical activity. Should this hold for the whole of Group IV., and as it has been shown to hold for nitrogen, the first member of Group V., all the elements of the latter group may be expected to act as optically active centres in appropriate compounds. Compounds of the types—



should therefore be optically active, R being an atom of any element in Group IV., and Q an atom of any element in Group V.

The application of the reactions now described to other elements is in progress, and the authors hope shortly to communicate results obtained with quadrivalent lead compounds.

25. "Note on the Refraction and Magnetic Rotation of Hexamethylene." By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

The specimen of hexamethylene obtained by one of the authors from Galician petroleum was found to contain a small quantity of a heptane. The hexamethylene was freed from the paraffin by fractional crystallisation, and its refraction and magnetic rotation were determined by Dr. W. H. Perkin, sen. The results obtained are given in the paper.

26. "Apiin and Apigenin. Part II. Note on Vitexin." By A. G. PERKIN.

By the action of nitric acid on apigenin under varied conditions, four nitro-derivatives have been obtained: *mononitro-apigenin*, $\text{C}_{15}\text{H}_9\text{O}_5(\text{NO})_2$, orange-yellow needles, m. p. about 302° , somewhat soluble in alcohol; *trinitro-apigenin* (a), $\text{C}_{15}\text{H}_7\text{O}_5(\text{NO}_2)_3$, yellow needles, m. p. about 296° ; *trinitro-apigenin* (b), yellow needles, m. p. $245-246^\circ$; and *tetranitro-apigenin*, $\text{C}_{15}\text{H}_6\text{O}_5(\text{NO}_2)_4$, almost colourless needles, m. p. $243-244^\circ$. With the exception of the first mentioned, all dissolve with difficulty in the usual solvents. In preparing the mononitro-compound, *dinitro-p-hydroxybenzoic acid* was obtained as a decomposition product, a further proof that apigenin does not contain a catechol group (*Trans.*, 1897, lxxii., 805). Tetranitro-apigenin appears to be identical with the compound $\text{C}_{15}\text{H}_6\text{O}_5(\text{NO}_2)_4$, obtained from vitexin (*Trans.*, 1898, lxxiii., 1026), and, as the decomposition products of both colouring matters are identical, vitexin must be a derivative of apigenin. The formulæ $\text{C}_{21}\text{H}_{20}\text{O}_{10}$ and $\text{C}_{21}\text{H}_{18}\text{O}_{10}(\text{C}_2\text{H}_3\text{O})_2$ are now assigned to vitexin and acetyl-vitexin, and it is suggested that vitexin is a *stable glucoside of apigenin*, and that a like constitution may also apply to scoparin (*Proc.*, 1899, xv., 123), which, according to this view, is a glucoside of a luteolin monomethyl ether.

Apiin, $\text{C}_{27}\text{H}_{32}\text{O}_{16}$, the glucoside of apigenin occurring in *Apium petroselinum*, is not converted by dilute nitric acid into nitro-apigenin, but into *nitroapigetritin*,

$C_{21}H_{27}O_{11}NO_2$, a yellow crystalline powder, very sparingly soluble in the usual solvents. This is the nitro-compound of a new glucoside, apigetrin, which differs from apigenin in containing but one sugar group. By prolonged digestion with dilute hydrochloric acid, it yields the above mononitro apigenin.

27. "The Yellow Colouring Principles of various Tannin Matters." VII. By A. G. PERKIN.

The yellow colouring-matter of the leaves of *Arctostaphylos uva-ursi* (bearberry) and *Hæmatoxylon Campeachianum* (logwood) is quercetin, and this is accompanied by a second substance, probably myricetin, to which the green colour of its alkaline solutions are due. Gallotannic acid occurs in some quantity in the latter leaves. The leaves of *Rhus metopium* contain gallotannin, myricetin, and a trace of quercetin, but the stem of this plant, unlike *R. cotinus* and *R. rhodanthema*, is devoid of colouring-matter. The sparing solubilities of acetylmyricetin and dibromquercetin have been employed for the separation of myricetin and quercetin. The leaves of *Robinia pseudacacia* contain a feeble colouring-matter, acacetin, $C_{16}H_{12}O_5$, which yields an acetyl derivative, $C_{16}H_{10}O_5(C_2H_3O)_2$, colourless needles, m. p. 195—198°, and on fusion with alkali phloroglucinol, p-hydroxybenzoic acid, and a trace of protocatechuic acid. Acacetin contains one methoxyl group, on removal of which a colouring-matter, $C_{15}H_{10}O_5$, results, having the reactions of apigenin. It is thus probably an apigenin monomethyl ether. The leaves of *Myrica gale* and *Coriaria myrtifolia* contain respectively myricetin and quercetin. Although a relationship frequently exists between the tanning and the colouring-matters of the same plant (*Trans.*, 1897, lxxi., 1138) there is no rule on this point, for exceptions are somewhat numerous.

28. "Note on the Bromo-derivatives of Camphopyric Acid." By J. ADDYMAN GARDNER.

An atom of hydrogen in camphopyric acid may be readily replaced by bromine, by the action of the halogen in the presence of phosphorus. Two acids of the formula $C_9H_{13}BrO_4$ are thus obtained, and are provisionally named α - and β -bromocamphopyric acid. These acids may be prepared either by treating camphopyric acid with phosphorus pentachloride, and subsequently warming with bromine, or by mixing the acid with amorphous phosphorus and adding the proper amount of bromine. In either case the product is poured into cold water, when part of the acid separates in the solid state and part is extracted with ether from the solution. The α - and β -acids may be separated by repeated crystallisation from benzene.

If only a small amount of water is used to decompose the acid bromides, bromocamphopyric anhydride is also obtained.

α -Bromocamphopyric acid separates from benzene or chloroform as a very light, white, crystalline powder, melting at 167° with previous softening. It is very moderately soluble in hot benzene and chloroform, but only slightly in cold; it is also very soluble in water, ether, acetone, and ethyl acetate. It is a dibasic acid, and forms very soluble sodium, barium, and ammonium salts.

α -Bromocamphopyric anhydride, $C_9H_{11}BrO_3$, may be obtained by treating the acid in the usual way with acetyl chloride or acetic anhydride. It crystallises readily from benzene in well-defined tabular crystals which melt at 226—227°. These crystals are very soluble in ether, acetone, and ethyl acetate.

β -Bromocamphopyric acid is more soluble in benzene than its isomeride, and is obtained, though in very small quantity, from the mother-liquors of the α -acid. It is a white crystalline substance melting at 207—208°, quite different in appearance from its isomeride. Its barium salt is soluble, and has the formula $Ba(C_9H_{12}BrO_4)_{2.4}H_2O$; this acid has not, however, been obtained in sufficient quantity for a more complete investigation.

The same products are obtained when camphoic acid

is similarly treated with phosphorus pentachloride and bromine.

α -Hydroxycamphopyric acid, $C_9H_{13}(OH)O_4$. If α -bromocamphopyric acid is heated for some time with a 10 per cent solution of potash, then acidified with hydrochloric acid and extracted with ether, an oily acid is obtained which for the most part solidifies on standing. If this be boiled with benzene the oily portion dissolves, and a white solid is left, which, on crystallisation from water, may be obtained in well-defined, colourless, transparent crystals which melt at 206—207°. This substance is a dibasic acid, and has the formula $C_9H_{14}O_5$. Its sodium and barium salts, which are very soluble in water, were analysed. It is only very slightly soluble in benzene, chloroform, and carbon bisulphide, but dissolves easily in ethyl acetate and in hot water; the oil obtained along with it is apparently an unsaturated acid, but has not yet been obtained in a state of sufficient purity for investigation. These substances are being prepared in quantity, and the author hopes before long to be able to bring before the Society a more complete account of their properties and reactions.

PHYSICAL SOCIETY.

Special Meeting, March 2nd, 1900.

Prof. G. CAREY FOSTER, F.R.S., Vice-President, in the Chair.

THIS Meeting was held, by invitation of Professor CALLENDAR, in the Physical Laboratory of University College.

DR. F. G. DONNAN read a paper on "The Relative Rates of Effusion of Argon, Helium, and other Gases."

The introduction to this paper contains a short account of the work which has been done on the effusion of gases. This is followed by a theoretical investigation of the subject, upon the assumption that the ideal gas laws are obeyed and that the back pressure never rises above a certain fraction of the internal pressure. This gives rise to formulæ which are different from the square root of the density law of Graham. The formula derived from Hugoniot and Reynolds' work gives the ratio of the times of effusion of two gases whose specific heat ratios are 1.408 and 1.67, equal to 1.06 times the square root of the ratio of the densities. The constant derived from Parenty's work is 1.084. The theory therefore indicates that argon should effuse faster than would be calculated from Graham's law. The gases used were oxygen, hydrogen, nitrogen, carbon-monoxide, carbon-dioxide, cyanogen, argon, and helium, and they effused through small holes pierced in platinum foil. When the holes are large compared with molecular dimensions, the phenomenon is one of efflux on a small scale. In the actual experiments this was the case, although the holes were sufficiently small to cause appreciable viscosity effects. By employing two or more observations in conjunction with the relative viscosities of the gases used, an apparatus constant was determined which allowed these effects to be eliminated. The observations showed that argon effused 3½ per cent faster than as calculated from the densities alone. This agrees qualitatively with theory, and affords a confirmation of the high specific heat ratio of argon. Hydrogen, oxygen, and carbon-monoxide effuse in the manner predicted by the theory for gases having the same or nearly the same specific heat ratios. Carbon dioxide, when compared with oxygen, appears to effuse 1 per cent faster than as calculated from the densities. This result is not in accordance with the adiabatic theory of the efflux of ideal gases. The results for helium are not uniform, but show that its behaviour is unlike that of argon, a result not foreseen by the theory. If account be taken of the deviation of ordinary gases from the ideal laws, it is

possible to obtain an expression for the efflux which contains a correction term involving the constant K of the Joule-Thomson effect. The sign of this correction term shows that a real gas will effuse more rapidly or more slowly than an ideal gas of equal density and specific heat ratio, according as K is positive or negative. The suggestion is made that possibly the anomalous results obtained with carbon-dioxide and helium may be thus explained. The deviations of the observed results from the results calculated for an ideal gas are, in the case of carbon-dioxide, in qualitative agreement with the theory proposed. In the case of helium they would be so if that gas possesses a negative K .

Lord RAYLEIGH congratulated the author and pointed out that in the case of very small apertures the gas laws might not be obeyed. The ratio of the dimensions of the aperture to the length of the mean free path determined this, and not the ratio of aperture to molecular dimensions.

Prof. RAMSAY and Prof. EVERETT expressed their interest in the work.

Dr. DONNAN thanked Lord Rayleigh for his correction, and stated that the apertures used were about $1/50$ m.m. in diameter.

Mr. E. C. C. BALY read a paper on "*The Distillation of Liquid Air and the Composition of the Gaseous and Liquid Phases.*"

From the experiments described in this paper the author has drawn curves showing the relation between the composition of the gas evolved by boiling liquid air and the temperature, and between the composition of the liquid and the temperature, both at constant (atmospheric) pressure. These curves enable the temperature of boiling liquid air to be at once accurately determined by means of an analysis either of the liquid or of the gas evolved. The measurements of temperature were made with a Callendar compensated constant pressure hydrogen thermometer. The correction for the contraction of the glass bulb was determined by measuring directly the linear expansion of glass between -190° and 20° C. This was found to be 0.0000073, Regnault's measurement between 0° and 10° being 0.0000085. The values for the boiling-points of oxygen and nitrogen agree fairly well with those given by Olszewski and Estreicher. Boiling nitrogen has a great tendency to superheat. This can be obviated by passing a rapid current through the boiling liquid, or by dropping in pieces of copper. There does not appear to be any connection between the ratio of the vapour-pressures and the composition of the gaseous phase in the distillation of oxygen and nitrogen at constant pressure. It is proposed to investigate the distillation at constant temperature.

Prof. RAMSAY drew attention to the uses of liquid air for carrying on researches at low temperatures. It is non-explosive, easy to work with, and is easily kept either by means of a vacuum jacket or by surrounding it with cotton-wool.

Prof. CALLENDAR referred to the question of superheating, and stated that the constant-pressure thermometer was more accurate than the constant volume one for measuring low temperatures.

A paper on "*The Reversibility of Galvanic Cells,*" by Mr. T. S. MOORE, was read by Dr. LEHFELDT.

In these experiments the reversibility of cells such as the Daniell and the Clark, which are assumed to be reversible, was tested by allowing the cell to send a current and by sending a current through the cell. The E.M.F.'s of the cells were determined by means of a Crompton potentiometer, and from the E.M.F.'s on open and closed circuits the internal resistance of the cells were calculated.

Prof. S. P. THOMPSON asked if experiments had been made upon Leclanché cells, where the products of the action escape.

Dr. LEHFELDT said that experiments were not made upon these cells, because they were known not to be reversible.

A paper on "*The Damping of Galvanometer Needles,*" by Mr. M. SOLOMON, was postponed until the next meeting.

The meeting then adjourned until March 9th.

NOTICES OF BOOKS.

Handbook of Practical Hygiene. By D. H. BERGEY, A.M., M.D. Easton, Pa.: The Chemical Publishing Company. 1899. Pp. 164.

THE practical hygiene of to-day has grown up from the observations and experience gained in many lands by various people. Most of these observations were made in the present century, as practically nothing had till then been done in advance of the rough methods of the ancients.

Most of the important work on water supplies in connection with certain diseases has been done in the last few decades, though much earlier the value of a sufficient air supply had been recognised by Howard, in regard to the high death rate in prisons. Besides plenty of air and a good water supply, modern sanitary science also takes note of the character of the soil with regard to dampness and porosity, or draining power.

Until the appearance of this volume there has been no short and concise laboratory guide to the subject published in English, though there are several treatises that cover the whole field, and a few handbooks in German.

The author may therefore reasonably expect a welcome to his work, which also includes, besides what we have already referred to, the elementary sanitary analysis of foods, and a chapter on ventilating and heating.

Lessons in Physical Chemistry ("Leçons de Chimie Physique") delivered at the University of Berlin, by J. H. VAN 'T HOFF. Translated from the German by M. CORVISY. Part II. Static Chemistry. Paris: Librairie Scientifique, A. Hermann. 1899. Pp. 162.

THE Lectures which form the subject of this volume were delivered by the author in the collegiate year 1897-98. Though forming the second part of the work, of which Dynamic Chemistry is Part I., this volume may also be considered an independent book, treating of the methods to which we owe what knowledge we at present possess of the size, structure, and grouping of molecules—methods which have given rise to the modern conception of the constitution of matter.

This volume is divided into three portions: Part I. on molecular weight and polymerism; Part II. on molecular structure (isometry, tautometry); Part III. on molecular grouping (polymorphism).

In volume I., besides the conception of the molecule, no hypothesis was needed on the nature of matter; in this volume the atomic hypothesis, on which depend the complex problems of structure, is introduced; while in the third volume, which is to follow, will be brought forward the still very obscure question of the relations between properties and composition, the whole forming a book of the highest value and interest.

A New Synthesis of Nitric Acid.—S. Tanatar.—The author has prepared nitric acid by reacting with sulphate of hydrazine dissolved in water on a 3.3 per cent solution of chloride of nitrogen in benzene. The two solutions are continuously shaken up together for two hours. The aqueous layer is then neutralised with soda, decanted, and supersaturated; a quarter of the liquid is distilled. The return is from 5 to 6.5 per cent. The best results are obtained by adding a little 10 per cent soda from time to time, until the alkaline reaction remains constant. The return is then 36 per cent, and could no doubt be still further increased.—*Berichte*, xxxii., p. 1399.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 7, February 12, 1900.

Researches on the Uric Series.—M. Berthelot.—The study of the uric series has of late years undergone a complete change. E. Fischer's theories on the fundamental radicle—purine—have caused the necessity of a further thermo-chemical examination of this series and extension of the interesting results obtained by M. Matignon. For an exhaustive study, this research would necessitate the preparation of thirty or forty new compounds discovered by M. Fischer. Without extending the work to this extent, the author found it possible to establish a certain number of essential relations, by choosing a series of typical substances for experiment. These were the glycollic and lactic nitriles, the indol derivatives, and xanthine. These compounds were used to establish two important thermo-chemical problems; especially the thermic effects of the addition of oxygen and those of the methylic substitution in the uric series.

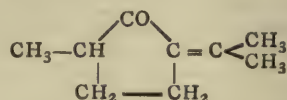
Dispersion of the Radium Rays in a Magnetic Field.—Henri Becquerel.—In a recent paper the author shows that the deviable portion of the radium rays are dispersed in a magnetic field. The deviated pencil being composed of radiation of which the trajectories are rays of different curvature, and of which the absorption across different screens varies with the nature and position of these screens. The author has improved the original experimental conditions, and obtained some results which are of assistance in the further study of these phenomena. Measurements have been taken with screens of paper, aluminium, mica, glass, platinum, copper, and lead.

Synthesis of Campholic Acid by means of Camphoric Acid.—A. Haller and G. Blanc.—A. Baeyer and V. Williger recently produced campholide by oxidising camphor by means of a solution of potassium persulphate in sulphuric acid. The authors have further effected the change of campholide into campholic acid. The campholide is first transformed into bromocampholic acid by saturating a solution of lactone in acetic acid with hydrobromic acid. The bromine derivative is precipitated little by little, the precipitation being completed in about twenty-four hours. This is collected on a filter, washed with acetic acid, and dried in a vacuum; this body is in the form of white crystals melting at 177°, and is identical with the substance which is obtained directly from camphor.

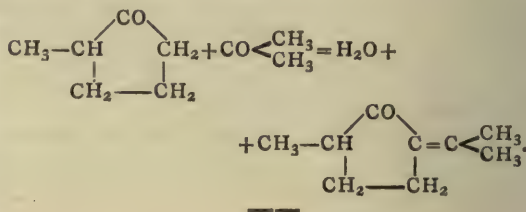
Composition of the Essence of Sandal Wood from the West Indies.—M. Guerbet.—The author was able to isolate the following definite compounds from sandal wood:—(1) Two sesqui-terpene carbides, $C_{15}H_{24}$. Sandalenes α and β , which are colourless oily liquids, with slight odour. Sandalene α boils at 252–252.5°, having a density of 0.9134 at 0°; it is lævo-rotatory $\alpha_D = -13.98^\circ$. Sandalene β boils at 261–262°, has density 0.9139 at 0°, and rotatory power $\alpha_D = -28.55^\circ$. (2) A mixture of sesqui-terpene alcohols, $C_{15}H_{26}O$, of rotatory power varying from $\alpha_D = -9.4^\circ$ and $\alpha_D = -25.3^\circ$, and corresponding absolutely to the preceding carbides. (3) An aldehyde of formula $C_{15}H_{24}O$, sandalal, a colourless liquid boiling at 180° at 40 m.m. pressure. (4) An acid of formula $C_{15}H_{24}O_2$, sandalic acid, obtained by oxidising sandalal with chromic acid in acetic solution. (5) Tere-sandalic acid, $C_{10}H_{14}O_2$, which crystallises from alcohol in large colourless prisms melting at 157°. (6) The most volatile portions of the essence, of strong odour, the author has not obtained in a state of purity.

Synthesis of the Phorone of Camphoric Acid.—L. Bouveault.—As a result of the work of W. Koenigs and

A. Eppens, the following formula was arrived at to express the phorone of camphoric acid:—



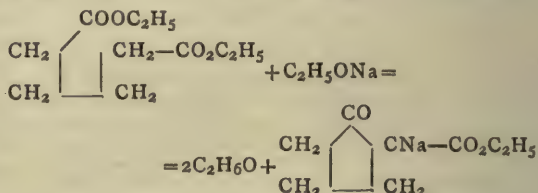
this being the generally accepted formula. The author synthesises this compound by condensing α -methylcyclopentanone—a substance he has previously synthesised—with ordinary acetone; the action appears to take place according to the equation—



Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 23.

On the Constitution Formula of Camphor.—L. Bouveault.—Not suitable for abstraction.

Synthesis of Cyclopentane Derivatives by means of Adipate of Ethyl.—L. Bouveault.—Most chemists now agree in making camphoric acid a cyclopentane derivative. The author thought it would be of interest to know what were the simplest bodies attached to this series; for this purpose he made use of a method described by M. Dieckmann, who condensed adipate of ethyl by means of ethylate of sodium according to the equation—



He did not isolate this β -ketonic ether, but he showed its existence by forming a copper salt. The cyclopentanone carbonate of ethyl is the simplest of the cyclic β -ketonic ethers, and was prepared by the author almost quantitatively as follows:—To one molecule of adipate of ethyl dissolved in its own weight of toluene is added one molecule of clean sodium, and the whole kept at 120–140° for four hours. The product, after cooling, is added to an excess of a 10 per cent solution of acetic acid. The oily layer contains toluene, cyclopentanone carbonate of ethyl, and a little unchanged adipate. These bodies can be separated by precipitating the ketonic ether in the form of a copper salt by means of a solution of acetate of copper. This result can be obtained more simply by shaking up the oil, first with an excess of 15 per cent potash, and then with strong potash; the mixed solutions are acidulated with acetic acid, the oil separated, washed with ether and carbonate of sodium, then, after driving off the ether, distilling in vacuo, when the desired ether is obtained in a state of perfect purity. Cyclopentanone-carbonate of ethyl is an oily, colourless liquid boiling at 113° under 22 m.m. pressure, $d = 1.0976$ at 0°. It has an acetylacetic odour, and answers to the formula $C_8H_{12}O_3$.

On the Natural Cyclisation of Citronnellal.—H. Labbé.—The author left a quantity of citronnellal in a nearly full flask for about two months. At the end of one month the odour was considerably modified. After sixty days the characteristic odour of citronnellal had com-

pletely disappeared, and was replaced by a strong smell of menthol. After shaking up with bisulphide to remove the unaltered citronellal it was rectified at the ordinary pressure. Nearly the whole passed over at 205–210°. Cyclic transformation was immediately suspected, but it could not have been effected by means of an acid agent; further, the alcohol obtained was free and not etherified. To identify this alcohol it was oxidised with a chromic mixture, and an oil boiling at 210° was obtained. The ketone thus obtained was transformed into a semi-carbazone in hydroalcoholic solution of chlorhydrate of semi-carbazide and acetate of sodium. After three days it was precipitated by water, and finally purified by crystallisation in ligroin. Its fusing point is 171–172°.

On the Formation of Citryl and Citronellyl-sulphites of Barium.—H. Labbé.—5 grms. of the normal sodic bisulphitic derivative of citral was dissolved in 150 c.c. of distilled water, at the same time 3 grms. of BaCl₂ were dissolved in 15 c.c. of water; on adding these two solutions together a voluminous precipitate is formed. This is filtered after half an hour, and the precipitate dried on a porous plate; it weighed 1.3 gm. Two hours afterwards, another precipitate was deposited, weighing in the same manner 0.35 gm.; finally, after forty-eight hours, a third precipitate was formed which also weighed 0.35 gm., the weight of the three thus being 2.0 grms. Theory requires 5.89 grms. In a second experiment 1 gm. of citronellylsulphite of sodium in 30 c.c. of water and 0.8 gm. of BaCl₂ in 8 c.c. of water were taken; the precipitate weighed 0.93 gm.; theory required 1.18 gm. This shows that when the bisulphitic derivative is sufficiently pure the precipitate is much more abundant, and exceeds 80 per cent of theory, whereas when not pure it may be as low as 17 per cent.

MISCELLANEOUS

The Tertiary Aromatic Amines.—C. Haeusermann and E. Bauer.—For examining the action of nitrous acid on the tertiary aromatic diamines, the authors have prepared some tetraphenylphenylene-diamines by the reaction of the dichlorbenzenes and diphenylamine soda. With *p*-dichlorbenzene they obtained two isomeric tetraphenylphenylene-diamines, one of them, α , purified by crystallisation in acetone, takes the form of brilliant colourless leaves, fusible at 199–200°, the other, β , is more soluble in acetone, and melts at 127–129°. The former, treated in acetic solution by nitrate of soda, gives a nitrated derivative, crystallised in brick-red needles fusible at 167–168°; the second, under the same conditions, gives a product crystallising in glacial acetic acid in brilliant yellowish-brown prisms, fusible at 185–186°. The formation of two isomers in the above case is no doubt due to the fact already observed by Istrati that *p*-dichlorbenzene becomes changed at a high temperature, into *m*-dichlorbenzene. While working with *o*-dichlorbenzene, the authors prepared tetraphenyl-*o*-phenylene-diamine, a crystalline powder, fusible at 133–134.5°.—*Berichte*, xxxii., p. 1912.

Preparation of α -Dinitrodimethylaniline.—J. Pinnow.— α -Dinitrodimethylaniline is obtained by means of dinitrochlorbenzene and dimethylaniline, or, according to Mertens, by means of dimethylaniline and dilute nitric acid: the best method is that of Schuster, which consists of operating with dilute nitric acid in the presence of a large quantity of sulphuric acid. The return did not, however, reach more than 90 to 110 per cent of the weight of dimethylaniline used, while theoretically we ought to obtain 174.4 per cent. The mother-liquors from the preparation of the α -dinitrodimethylaniline contain a fairly large quantity of *o*-dinitrodimethylaniline. The

author has determined the character of this base, which is in the form of a reddish oil, by preparing its picrate, which crystallises in fine prisms, fusible at 102–103.5°: *o*-amido-dimethylaniline, obtained by the reduction of the *o*-nitro by means of Zn+HCl, is an oil distilling at 217.5° under a pressure of 715 m.m., having the smell of menthol. Fe₂Cl₃ gives a cherry-red colour to its alcoholic solution. Its hydrochlorate occurs in white prisms, fusible at 184–186°; its picrate in leaves fusible at 138–140°. The acetyl derivative appears in fine white needles, fusible at 72–73°. Heated for half-an-hour with double its weight of acetic anhydride, to 160°, it gives *N*- α -dimethylbenzimidazol.—*Berichte*, xxxii., p. 1666.

Deviation of the Becquerel Rays in the Magnetic Field.—F. Giesel (*Wied. Ann.*, No. 12, 1899) shows that these rays are deviated by magnets. A preparation of polonium was the source of the rays. Radium also showed the same phenomenon but not to so high a degree.—*Am. Journ. Sci.*

Preparation of Pure Tertiary Anilines and Tetra-alcoylised Aromatic Diamines.—J. Pinnow.—The author found in the use of warm ammonia a simple means for the preparation of the tertiary anilines, the tetra-alcoylised aromatic diamines, the dimethyl-amido phenols, the dimethylamidobenzoic acids, &c., from their halogeno-alcoylised products of addition; it is only necessary to obtain an alcoylation as advanced as possible, and to remove the impure tertiary bases from the product of the reaction before using the ammonia. Some observations were made during this research which recall the work of Bischoff and Menschutkin; we know that these chemists found that certain groups interfered with the complete alcoylation of the base, probably on account of their stereo-chemical character. Thus the addition of a halogen-alcoyl to the tertiary anilines in which the ortho-position relative to an amido-group is occupied, offers certain difficulties; it is therefore necessary to modify the conditions of the reaction according to the case presented. The number of basic or acid groups also plays an important role in the separation of the halogeno-alcoyl by means of ammonia; a temperature of 110–140° suffices in the case of monamines and of amido-carbonic acids, for example, while for diamines and the amido-phenols it is necessary to heat to above 140°, preferably to 180–190°. The time of heating is generally an hour at 180–190°, and two or three hours at 130–140°; the ammonia is transformed into mono-, di-, or trimethylamine. Experiments were made with the three phenylene-diamines, with benzidine, ortho-amido-phenol, *p*-amido-benzoic acid, and with the naphthylamines.—*Berichte*, xxxii., p. 1401.

The Preparation of Crystallised Calcium.—Henri Moissan.—Crystallised calcium can be prepared by two methods. To obtain it in a state of purity the author made use of the property, hitherto unknown, of dissolving it in liquid sodium kept at a dull red heat. On cooling, the calcium crystallises out, and, by treating the metallic mass with absolute alcohol, brilliant white hexagonal crystals of pure calcium remain. 600 grms. of anhydrous crystallised iodide of calcium are placed, with 240 grms. of sodium, in an iron crucible of 1 litre capacity; this is closed with a screw-down cover, and heated to dull redness for an hour. On cooling, the crucible is found to contain a layer of melted salt of a blue colour, covered by a cake of metallic sodium. This sodium, broken up to fragments of about 1 c.c., is added to 500 c.c. of anhydrous absolute alcohol, kept at 0° in a 1 litre flask. The return of calcium is about 50 per cent of the theoretical amount. Similar crystals of calcium can be obtained by the electrolysis of melted iodide of calcium at a dull red heat. The negative electrode is of pure nickel and the positive of graphite. Under these conditions a white melted, or crystalline, metal is obtained.—*Bull. Soc. Chim.*, Series 3, xxi., Nos. 20–21.

On the Percarbonates.—S. Tanatar.—The author has obtained percarbonates by reacting with H_2O_2 on Na_2CO_3 or K_2CO_3 . These percarbonates, heated to 100° , do not give off oxygen, while those prepared by the electrolytic method by Hansen and Constam give off both CO_2 and O . Percarbonate of soda should correspond to the formula, $\text{Na}_2\text{CO}_4 + 1\frac{1}{2} \text{ aq.}$ This salt is gradually decomposed in aqueous solution, into H_2O_2 and Na_2CO_3 ; when an acid is added there is a disengagement of CO_2 , and the solution retains H_2O_2 , which can, however, be extracted with ether. The author, to make certain that he had not to do with a mixture of Na_2CO_3 and H_2O_2 , determined the heat of decomposition of the salt by nitric acid, and he found the number of calories ($7210-7260$) higher than that required by the decomposition of Na_2CO_3 (533 cal.). Percarbonic acid is thus a weaker acid than carbonic. He has not succeeded in obtaining pure percarbonate of potassium. With metallic salts the sodium salt gives precipitates, which easily decompose with the evolution of oxygen, so that it has not been possible to prepare the corresponding percarbonates.—*Berichte*, xxxii., p. 1544.

MEETINGS FOR THE WEEK.

- MONDAY, 12th.**—Society of Arts, 8. (Cantor Lectures). "Photography of Colour," by E. Sanger Shepherd.
- TUESDAY, 13th.**—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
- Society of Arts, 8. "English Furniture," by Laseby Liberty.
- WEDNESDAY, 14th.**—Society of Arts, 8. "Continuation School Work in Rural Districts," by H. Macan, M.A., F.C.S.
- THURSDAY, 15th.**—Royal Institution, 3. "Recent Excavations at the Argive Heraeum (in Greece)," by Charles Waldstein, Litt D., Ph.D., L.H.D.
- Chemical, 8. "The Vapour Densities of Dried Mercury and Mercurous Chloride," by H. Brereton Baker, M.A. "The Preparation of Pure Hydrobromic Acid" and "A New Sulphide of Arsenic," by A. Scott, D.Sc., F.R.S. "The Action of Iodine on Alkalies," by R. L. Taylor. "The Interaction between Sulphites and Nitrites," by Edward Divers, D.Sc., F.R.S., and Tamemasa Haga, D.Sc. "New Polysaccharides—Manno-galactan and Lævulo-mannan," by Julian L. Baker and Thomas H. Pope.
- FRIDAY, 16th.**—Royal Institution, 9. "Pictorial Historical Records," by Sir Benjamin Stone, M.P.
- SATURDAY, 17th.**—Royal Institution, 3. "Polarised Light," by The Rt. Hon. Lord Rayleigh, M.A., D.C.L., &c.

Required immediately, a Senior and a Junior Chemist for important old-established Explosive Works. Must have had practical experience with Nitro-glycerin and Blasting Compounds, Cordite, and other specialities. State where at present or last employed, age, salary expected, and full particulars. Applications will be treated in strict confidence.—Write, "Explosives," care of Street's Agency, 30, Cornhill, London, E.C.

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TECHNOLOGICAL EXAMINATIONS, 1900.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2103.

RADIATION FROM RADIO-ACTIVE BODIES.

By HENRI BECQUEREL.

THE author obtained, from M. and Mme. Curie, a specimen of polonium nitrate which was nearly as radio-active as radium, whether measurements were made on the increase of conductivity of air or on the action on a photographic plate.

The radiation from this substance appeared to be unaffected by a magnetic field, so differing from radium radiation.

The polonium is placed between the poles of an electro-magnet, in a magnetic field of intensity 4000, and above it a photographic plate, not enclosed in a black envelope on account of the absorption of polonium rays by black paper. After some minutes a symmetric impression will be found on developing the plate, and this impression is the same whether the electro-magnet is excited or not.

If radium is substituted for polonium, the experimental conditions remaining the same, a non-symmetric impression is found on the plate when the magnet is excited, showing that the rays have been shifted in the direction of the current, producing the field.

In a previous paper the varying penetration of polonium and radium rays with regard to different substances has been discussed. From consideration of the experiments described in this paper and previous work, the author arrives at the conclusion that the radium rays resemble cathode rays to a certain extent, but have not all their properties. For example, if, in a magnetic field which has been rendered practically uniform, a small quantity of radium is placed on a photographic plate enveloped in black paper, horizontal and parallel to the field, then at right angles to this is placed a second plate, whose position with regard to the radiant source and the pole pieces varies in different experiments. After some moments, on developing the horizontal plate, curves are found, which have been described in a previous paper, whilst on the vertical plate is an intense impression limited by a spiral in the direction of the current which produced the field.

These experiments allow of the measurements of the deviation in a magnetic field.—*Comptes Rendus*, 1899. vol. cxxix., No. 26.

THE ACTION OF MERCURY ON IODIDE OF METHYLENE.

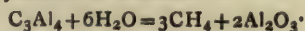
By V. THOMAS.

WHILE the organo-metallic derivatives in which the metallic bonds are saturated by monovalent radicals have long been studied, such is not the case with the organo-metallic derivatives, which can be foretold theoretically by substituting for several hydrogen atoms of a carbide, di-, tri-, and tetra-valent metallic atoms.

In the hope of isolating some metallic compounds of olefiant gas, Messrs. Wanklyn and Von Than studied the action of mercury and zinc on iodide of ethylene, but they were unable to arrive at the wished-for goal. In 1880 Sakurai took up their experiments, but substituted chloride, bromide, and even chloriodide of ethylene, for the iodide; unfortunately he was no more successful than his predecessors. He had, however, the idea of re-

placing the ethylenic halogen compounds by iodide of methylene. On leaving iodide of methylene and metallic mercury in contact in a sealed tube, in the presence of a small quantity of mercurous iodide, he observed that after four or five days the contents of the tube were transformed into a yellowish-white mass, which further took a red colour after a longer time. On opening the tube no trace of gas was noticed. The product of the reaction consisted principally of two compounds, one of which dissolved easily in iodide of methylene; the other, on the contrary, was quite insoluble in this body. The soluble compound consisted, according to this authority, of the derivative $\text{CH}_2\text{I.HgI}$. The insoluble derivative was not analysed.

More recently M. Moissan (*Bull. Soc. Chim.*, Series 3, vol. xx., p. 1010) has prepared the carbide of aluminium, C_3Al_4 . On decomposing this body by water, he effected a remarkable synthesis of methane:—



From this it follows that this carbide of aluminium corresponds to the formula $\text{Al}\equiv\text{C}-\text{Al}=\text{C}=\text{Al}-\text{C}\equiv\text{Al}$, and constitutes the first organo-metallic derivative known, in which each bond of the metal is not saturated by a monovalent carbonated radical.

The research I have undertaken had for its object to determine the behaviour of the different metals with iodide of methylene; I thought it would be first of advantage to repeat Sakurai's experiment.

Action of Mercury on Iodide of Methylene in the Cold.—By leaving $\text{Hg.Hg}_2\text{I}_2$ and CH_2I_2 in contact for several days I obtained the compounds described by Sakurai, but the mercurous iodide, contrary to what was said by that chemist, does not appear to play any rôle at all. In fact, the reaction is quite identical if we proceed without this salt.

In a future paper I shall return to the compounds thus obtained.

Action of Mercury on Iodide of Methylene when Warmed.—If, instead of proceeding at the ordinary temperature, we use heat, the reaction becomes more rapid; but after a certain temperature gaseous products are given off. I have studied the reaction at about 200°. For this purpose 40 grms. of mercury were heated with 22 grms. of iodide of methylene to between 190° and 200° for ten or twelve hours in a sealed tube. After the reaction the tube contains large crystals of mercuric iodide, some red and others yellow. The liquid has completely disappeared.

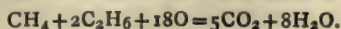
The gases given off are collected over mercury, and submitted to the following tests:—

1. Treatment by potash; no absorption.
2. Treatment by pyrogallic acid; no absorption.
3. Treatment by acid cuprous chloride; no absorption.
4. Treatment by bromine; no absorption.
5. Treatment by fuming sulphuric acid; no absorption.
6. Treatment by ammoniacal cuprous chloride; no absorption.

Eudiometric analysis gave the following figures:—

Taken as sample	2'27 c.c.
Oxygen added	8'22 "
Volume after sparking	6'1 "
" " absorption by KOH	3'1 "
Remainder not absorbed by pyrogallic acid	0'44 "
Oxygen not used	2'75 "

As we find, from preliminary tests, that the gases formed belong to the series of saturated carbides, the analytical results lead us to consider them as a mixture of methane and ethane in the proportion of $\text{CH}_4 + 2\text{C}_2\text{H}_6$. In fact, the reaction of the combustion is as follows:—



This reaction shows that 1 volume of carbide ought to give 2'6 volumes of steam and 1'6 volumes of carbonic

acid. The figures found by analysis are $H_2O=2.4$ vols., and $CO_2=1.6$ vols.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 2.

mercury, with carbonate or borate of soda added, as proposed by M. Denigès.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 12.

A NEW METHOD FOR THE ESTIMATION OF CYANIDE OF MERCURY.

By E. VINCENT.

THE estimation of cyanide of mercury offers certain difficulties, owing to the great stability of the salt. It may be effected in the following manner:—

A. Precipitation of the mercury in the state of sulphide in the cyanide solution, to which an ammoniacal solution of nitrate of zinc has been added, and estimation of the mercury after solution in *aqua regia*.

B. Estimation of the cyanogen in the form of cyanide of silver, in the solution from which the mercury has been removed.

This method gives very good results, but it requires long and careful manipulation. It appeared to me to be desirable to find a more rapid method, without sacrificing efficiency.

The principle of the method is as follows:—When cyanide of mercury is heated with soda-lime, the mercury is set free in the metallic state, and the nitrogen is converted into ammonia. By collecting and weighing the mercury, and, on the other hand, collecting the ammonia in titrated sulphuric acid, we can simultaneously estimate the mercury and the nitrogen.

As can be seen, the method consists entirely in combining the two processes, the one for the estimation of the mercury (action of lime on mercurial compounds), and the other for the estimation of the nitrogen in certain organic compounds (Will and Varrentrapp's method).

Experiment has shown that it can be perfectly well applied to the case in question.

I have experimented on samples of perfectly pure cyanide, and I have also made comparative tests with the ordinary method and the soda-lime method.

In the following table I give some of the results obtained:—

		Found.	Calculated for $Hg(CN)_2$.
		$Hg=78.5\%$	$Hg=79.3\%$
Sample No. 1.	Ordinary method ..	$N=10.99\%$	$N=11.11\%$
	Soda-lime method ..	$Hg=78.3\%$	—
Sample No. 2.	Ordinary method ..	$N=10.91\%$	—
	Soda-lime method ..	$Hg=78.3\%$	—
		$N=10.91\%$	—
		$Hg=78.4\%$	—
		$N=10.89\%$	—

The method is very rapid, and the above results show that it is perfectly applicable.

In practice cyanide of mercury is easily obtained in a pure state, and does not often need to be tested. Such, however, is not the case with commercial oxycyanides, and it is especially in this direction that the above described method will be useful.

I have estimated a certain number of samples of oxycyanide, and I obtained extremely variable results. One sample gave results very close to those of pure oxycyanide; some have a composition which decidedly resembles that of cyanide of mercury, while others appear to be mixtures of various proportions of cyanide of mercury and mercuric oxide.

These variable results obtained with the oxycyanides show that the substitution of the oxycyanide for the cyanide, in the sterilising of surgical instruments, is quite possible.

It might perhaps be preferable to use simply cyanide of

ACTION OF HYDROCHLORIC ACID GAS UPON SULPHATES, SELENATES, TELLURATES, AND PHOSPHATES.*

By RAYMOND W. TUNNELL and EDGAR F. SMITH.

EXPERIMENTS have been made at various times in this laboratory upon the action of the gaseous haloid acids on metallic oxides and sulphides. Frequently new methods of separation have resulted. These have proved very satisfactory in every respect, from the standpoint of the analyst.

In the following paragraphs we give additional data collected from the same field, and trust that they may not be devoid of interest to the reader.

Knowing that selenic and telluric acids could not be expelled from their salts by hydrochloric acid gas we endeavoured to ascertain whether, if a sulphate were mixed with one or both of the preceding salts, it would be possible to drive out the selenic or telluric acid and leave the sulphate intact. Accordingly a perfectly dry mixture of a sulphate and a selenate was exposed to the action of well-dried hydrochloric acid gas. The selenic acid was not only expelled, but also varying amounts of sulphuric acid were driven out. Thus, two trials were made with definite amounts of the salts. The results are these:—

Potassium sulphate taken.	Potassium selenate taken.	Sulphur remaining in the salt acted upon.
Grm.	Grm.	Per cent.
0.4323	0.4567	33.59
0.3338	0.1583	33.51

In brief, about 65 per cent of the sulphur originally contained in the potassium sulphate was expelled in the presence of the selenate. When a tellurate was mixed with the sulphate and the two subjected to the action of hydrochloric acid gas, not only was the tellurium driven out from its combination, but the sulphur also in amounts which varied with the working conditions. The original idea therefore of effecting a separation was abandoned.

We next exposed pure, dry potassium sulphate to the influence of the haloid acid. A weighed amount of the salt was introduced into a porcelain boat, placed in a combustion tube of hard glass, through which the gas was conducted in the cold. It was very soon observed that the salt had increased very considerably in weight (as much as 12 per cent). After a time the boat was removed and the residue in it analysed. Thus, 1.0896 grms. of potassium sulphate after exposure for three and one-half hours to the gas, in the cold, weighed 1.1162 grms.—an increase of 0.0266 gm. The salt was dissolved in water, and the hydrochloric acid in it determined. It equalled 0.0268 gm., or a difference of 0.0002 gm. from the observed increase in weight. This product (an addition product evidently) maintained its composition when exposed to 130° in a drying oven. It did not lose in weight on standing over soda-lime, in a vacuum desiccator, for fifteen hours.

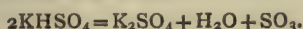
When dry potassium sulphate was heated in hydrochloric acid gas from 200° to a dull red heat, an examination of the water in the receiving vessel showed the presence of sulphuric acid, while the substance remaining in the boat after this treatment weighed more

* Contribution from the John Harrison Laboratory of Chemistry. From *The Journal of the American Chemical Society*, vol. xxi., No. 10.

than the original substance. It gave an acid reaction to litmus, and decolourised a red phenolphthalein solution. As much as 19 per cent of the sulphuric acid in the salt was expelled in this way. The quantity of acid driven out was greater in the presence of a selenate or tellurate, equalling in several instances 75 per cent.

This deportment of sulphuric acid confirms an early observation of Heusgen (*Ber. d. Chem. Ges.*, 1876, 1671), who found that "Kalium sulfat wird weder in der Kälte noch bei gewöhnlicher Temperatur von Salzsäure angegriffen . . . bei 360 liess sich in dem vorgelegten Wasser schon eine wägbare Menge Schwefelsäure nachweisen, bei dunkler Rothgluth erfolgt jedoch die Zersetzung fast quantitativ in Chlormetall und freie Schwefelsäure." The gas evidently attacks the salt in the cold. This is proved by the formation of the addition product. We never observed a complete elimination of the sulphuric acid. It was not, indeed fast "quantitative." And, Prescott (*CHEM. NEWS*, xxxvi, 178), trying the action of aqueous hydrochloric acid upon metallic salts, observed that upon evaporating a grm. of sodium sulphate with 4.035 grms. of aqueous hydrochloric acid, containing 1.251 grms. of hydrochloric acid, he obtained only 0.070 grm. of sodium chloride, and 0.807 grm of undecomposed sulphate remains.

The question as to how the sulphuric acid is expelled from its salt is worth consideration. The thought first suggested was that the addition compound, $K_2SO_4 + HCl$, is produced when the gas acts upon the salt, and this upon the application of heat decomposes, forming potassium chloride and acid potassium sulphate, the latter being changed by the same heat into—



If this were true then the addition compound, which in theory was formed at first, when heated alone in dry air should give up its sulphuric acid in part at least, and it should be found in the water of the receiver. Several trials were made. Sulphuric acid was not found in the receiver, but instead about 86 per cent of the hydrochloric acid originally present with the potassium sulphate was discovered to be there. After numerous experiments of various sorts we concluded that this remarkable expulsion of sulphuric acid from one of its stable salts is to be attributed to mass action. This is emphasised by its more complete expulsion when a selenate or a tellurate is present.

It is a well-established fact that phosphoric acid is not expelled by the gaseous haloid acids from its salts.

A mixture of dry sodium tellurate and dry sodium pyrophosphate was exposed to the action of hydrochloric acid gas. Care was taken that the temperature did not become so intense as to melt the mass in the boat. When this occurs the telluric acid is apparently reduced very rapidly. In the analysis, which will be introduced, the tellurium was merely expelled. No attempt was made to estimate its amount. The residual phosphate, after solution in water, was invariably examined for tellurium, but it was not detected. The phosphoric acid was determined in the usual manner.

Analyses.

	Phosphorus present in the $Na_2P_2O_7$.	Amount of sodium tellurate taken.	Phosphorus found as $Mg_2P_2O_7$.
	Grm.	Grm.	Grm.
1.	0.1030	0.1247	0.1026
2.	0.1197	0.1632	0.1199
3.	0.1096	0.0832	0.1094

Sodium selenate was next mixed with sodium pyrophosphate. Much less time was required for the volatilisation of the selenic acid than for that of the telluric acid. The temperature was gradually raised to 450° C. It was not allowed, nor was it necessary, to go beyond this point.

Analyses.

	Phosphorus present in the $Na_2P_2O_7$ used.	Sodium selenate.	Phosphorus found as $Mg_2P_2O_7$.
	Grm.	Grm.	Grm.
1.	0.0728	0.1763	0.0729
2.	0.1057	0.2017	0.1054
3.	0.1198	0.1416	0.1199

The preceding results with phosphates and tellurates and those with selenates and phosphates leave no doubt as to the complete separation of their respective acids, in the manner indicated. The method is free from all disturbing factors and may be executed without difficulty.

NOTES ON THE ANALYSIS OF DYNAMITE AND GELATIN-DYNAMITE.

By F. W. SMITH.

I.

The analysis of dynamite is not often described in textbooks, and the following notes, gleaned from some years' experience, may be of interest to those who have occasion to investigate such products.

A simple case is that of a dynamite containing nitro-glycerin, sodium nitrate, wood-pulp, and basic magnesium carbonate or kieselguhr. The following process of analysis is recommended as giving satisfactory results:—Weigh out 10 grms. on a pair of watch-glasses, place in a desiccator over sulphuric acid, and leave for at least five days. The loss in weight is called moisture. Weigh about the same amount into a Gooch crucible and extract with pure ether. A drop of the ether is allowed to evaporate on a piece of tissue paper from time to time, and the extraction continued until the paper no longer tastes of nitro-glycerin. Dry the residue in an air-bath at about 80° C. for two to three hours, and weigh. The loss minus the moisture is called nitro-glycerin. In the case of powders containing only nitro-glycerin and kieselguhr, this extraction is considerably more difficult, and it is advisable to remove the dynamite from the Gooch crucible to a small beaker and stir up with ether, washing the residue back when free from nitro-glycerin. After extracting the nitro-glycerin, the nitre is extracted with cold water, and after the water ceases to extract anything it is displaced by acetone with the object of drying the residue without affecting the starch if any be present. The loss in weight is called sodium nitrate, potassium nitrate being very rarely used. The residue from the water extraction is ignited until free from carbon. The loss is wood-pulp, flour, bran, &c. I have found no satisfactory method for separating these, and rely on testing with iodine for the presence of starch as an indication of the presence of flour, &c.

If no earthy absorbents have been used, the ash after ignition is not likely to be over one-tenth per cent of the whole sample. If the ash is considerable it is extracted with hydrochloric acid, and the residue dried. The loss, expressed in percentages, is subtracted from the percentage of loss on ignition. The loss on ignition minus the loss on extraction with hydrochloric acid is called wood-pulp, &c., while twice the latter is entered as basic magnesium carbonate. This method saves a quantitative determination of the magnesia in the extract and rests on the fact that the basic magnesium carbonate employed as an absorbent loses practically one-half its weight on ignition. The extract should, however, be examined for lime, &c.; a small amount of iron may come from the kieselguhr. If any residue be left after extracting with hydrochloric acid it is examined under the microscope for kieselguhr, mica, &c., or it may be a small amount of venetian red used for colouring the powder.

The following analysis will serve to illustrate the methods:—

No. 515.	Per cent.	Per cent.
Moisture	1.3	—
Nitro-glycerin	39.6	39.6
Sodium nitrate	46.8	47.1
Wood-pulp	9.5	—
Basic magnesium carbonate ..	1.8	—
Kieselguhr	1.0	—
	100.0	

The loss on ignition was 10.40 per cent, and on extraction with hydrochloric acid 0.90 per cent. A quantitative determination of the magnesia, calculated as $Mg(OH)_2 \cdot 3MgCO_3 \cdot 3H_2O$, gave 1.8 per cent. The portion used for moisture determination may be used to check the extractions.

Lunge's nitrometer may be used to advantage as a check on the analysis. About $\frac{1}{4}$ grm. of the dynamite is weighed into a small weighing bottle and about 10 c.c. of pure sulphuric acid poured over it. It is then allowed to stand from twelve to eighteen hours. In this time the whole usually goes into solution. In the cold the reaction is perfectly calm and no nitrogen is lost. It is then introduced into the nitrometer and decomposed as usual. The result is most conveniently expressed in cubic centimetres of nitric oxide per grm. On the sample mentioned above three determinations in the nitrometer gave 237.0, 234.5, and 236.5 c.c. of nitric oxide per grm. 39.6 per cent of nitro-glycerin gave 116.9 c.c., 46.8 per cent of sodium nitrate gave 122.9 c.c. of nitric oxide per grm. respectively; total, 239.8 c.c. The sodium nitrate used is generally 96 to 98 per cent pure; assuming 97 per cent reduces the calculated c.c. to 236.1. The nitrometer work shows that in this case the ether-soluble portion contains nothing but nitro-glycerin, the water-soluble portion nothing but sodium nitrate and its usual slight impurities. Eight minutes agitation in the nitrometer is sufficient for almost all cases.

II. Gelatin-dynamite.

The gelatin-dynamites are considerably more difficult to analyse. The following analysis may be selected as typical:—

No. 478.	Per cent.
Moisture	0.4
Nitro-glycerin	33.7
Sulphur	1.9
Resin	7.0
Sodium nitrate	54.0
Gun-cotton	1.1
Wood-pulp	1.9
	100.0

The sample for moisture is weighed out as before. A filter cone (C. S. and S.) is dried and weighed in a weighing bottle and about 15 grms. of the powder weighed into it. This is extracted in a Soxhlet apparatus with chloroform. The loss includes nitro-glycerin, sulphur, and resin. Sometimes the powder melts together in the hot chloroform, and in that case it must be taken from the filter and broken up in a beaker with cold chloroform until the bulk of the nitro-glycerin is dissolved. After extracting with chloroform the residue is extracted with cold water to remove the sodium nitrate, dried and weighed, then extracted with acetone, and the loss on extraction with acetone called gun-cotton. The still remaining portion consists of wood-pulp and earthy absorbents which are treated as above described. Sodium nitrate is appreciably soluble in acetone, and should, on that account, be removed before the gun-cotton. It is often recommended to extract with acetone first and precipitate the gun-cotton with chloroform. This method gives results which are too high, because the sodium nitrate dissolved by the acetone is also precipitated along with the gun-cotton. Allowance for this can, however, be made by incinerating the gun-cotton and calculating the ash as sodium nitrate.

The second and following extractions can conveniently be made in the filter cone, setting it in a test-tube with perforated bottom. The filter is finally incinerated in a platinum dish with the residue, allowance being made for its ash content, which in one case was 11.4 m.grms.

The chloroform solution is evaporated almost to complete absence of chloroform and taken up with glacial acetic acid. The precipitated sulphur is washed into a weighed Gooch crucible, and washed further with a little strong alcohol to remove the resin. The nitro-glycerin is determined by weighing a suitable portion of the powder (in this case 1.8 grms.) into a small beaker. Ether is then poured on, and the powder worked over with a platinum spatula. The ether is several times renewed, being poured on a filter and collected in a glass evaporating dish. The ethereal solution is allowed to evaporate spontaneously in a cool place, the dish being covered with tissue paper. After twelve hours the residue can be washed into the nitrometer with acetic acid, care being taken not to use too much acetic acid, which retards the reaction of decomposition, while if too little be used the reaction may be extremely violent. Even with the greatest care in evaporation some nitro-glycerin is lost, and the results are usually about 1 per cent low.

The calculated c.c. of nitric oxide per grm. on this analysis, assuming the gun-cotton to contain 11.9 per cent of nitrogen, are 99.5 for the nitro-glycerin, 141.7 for the sodium nitrate, and 2.7 for the gun-cotton; total, 243.9. Two determinations in the nitrometer gave 243.8 and 242.7. As the sodium nitrate was certainly not pure, this result shows that the figure entered for nitro-glycerin must be too low. Assuming the sodium nitrate to be 98 per cent pure gives 138.9 c.c., and this, plus 2.10 c.c. for the gun-cotton, subtracted from 243.2, total by analysis, gives 102.2 c.c. for the nitro-glycerin, corresponding to 34.6 per cent. Of course, if necessary, the water-soluble portion could be isolated and estimated in the nitrometer. The amount given in the analysis, 33.7 per cent, was determined by analysing the ether-soluble portion in the nitrometer and calculating the nitric oxide obtained as $C_3H_5N_3O_9$. The resin in this case was recognised by its odour, and estimated by difference. An attempt to determine it in alcoholic solution, in presence of nitro-glycerin, by titration with alcoholic potash, failed because nitro-glycerin by itself is decomposed by alcoholic potash, decolorising phenolphthalein solution. Some so-called flameless dynamites contain ammonium nitrate. The ammonia is estimated by distillation from aqueous solution and calculated as nitrate.

The two examples given cover the great bulk of dynamites and gelatin-dynamites used in the United States, but many other mixtures, often of a very fanciful nature, are occasionally encountered, some of them exceedingly difficult if not impossible to analyse. The methods of analysis given in Guttman's "Manufacture of Explosives," vol. II., are mainly reliable as far as they go, while some of Sanford's methods are likely to lead to disappointment. His separation of nitro-glycerin from camphor is especially difficult to understand, since nitro-glycerin and carbon disulphide mix completely on the addition of camphor.

It is hoped that this paper will provoke discussion which may lead to the adoption of uniform methods of analysis by the chemists who have to deal with this class of products.

III. Various Notes.

The nitrometer is conveniently set by the use of pure potassium nitrate. Exactly $\frac{1}{4}$ grm. is weighed into a weighing bottle, covered with sulphuric acid, and allowed to stand until the solution becomes clear. The nitric oxide from this is brought into the measuring tube, and the amount of air in the reduction tube, which should also contain a few drops of water, is varied until the gas in the measuring tube shows 110.5 c.c. with the air in the reduction tube at 100 c.c. The use of potassium nitrate

eliminates a large number of errors, such as those of reading the barometers, thermometers, &c. The potassium nitrate may be purified by dissolving it in the least possible quantity of cold water and precipitating with an equal volume of pure alcohol. Three times is generally sufficient, and the absence of chlorides and sulphates may be taken as a criterion of purity. Sodium nitrate, made by dissolving sodium in alcohol and neutralising with dilute pure nitric acid, may be used as a check on the potassium nitrate. Leaky stopcocks are a frequent source of annoyance in working with the nitrometer. The stopcock of the measuring tube may be tested each time by allowing it to stay open for an instant after connecting it to the decomposing bulb by means of a thick-walled rubber tube and allowing the mercury reservoir to be at its lowest position. The mercury should not sink in the measuring tube. This assures the tightness of everything from the lower side of the stopcock in the measuring tube to the upper side of the stopcock in the decomposing bulb. The stopcock in the decomposing bulb may be tested by analysing the standard potassium nitrate, first with the level of the mercury in the reservoir about 6 inches above that in the decomposing bulb, and secondly about 6 inches below. If the first analysis shows too low a result, and the second too high, it points conclusively to a leak. A person having much nitrometer work to do must familiarise himself with the grinding of stopcocks, as they rarely leave the manufacturers' hands in a perfect condition. Grease for the stopcocks is made from vaseline with the addition of Japan wax and rosin, the proportions being varied in summer and winter to get a product of suitable hardness and consistency.

The refraction method for the valuation of Chili nitre gives results from 1 to 1½ per cent higher than those obtained by using the nitrometer and calculating the nitric oxide obtained as sodium nitrate. This is due to the almost unvarying presence of potassium nitrate, and the occasional presence of potassium perchlorate. The latter may be determined by fusing at a low temperature in the presence of powdered cupric oxide. The increase of chlorides after fusion is calculated as potassium perchlorate. The following is a complete analysis of one sample:—

No. 471.	Per cent.
Moisture	2.2
Insoluble	0.1
Magnesium sulphate	0.2
Magnesium chloride	0.1
Sodium chloride	0.4
Potassium nitrate	3.6
Sodium nitrate	93.4
Potassium perchlorate	0.0
	100.0

The refraction method gave 96.8 per cent of sodium nitrate by difference.—*Journal of the American Chemical Society*, xxi., No. 5.

THE SPECIFIC GRAVITY OF CÆSIUM.

By A. E. MENKE.

THE specific gravity of cæsium was determined many years ago by Settleler and given as 1.88. He, however, worked with relatively small quantities of the metal (0.6 and 1.1 grm.), as his method of preparation did not allow him to obtain cæsium in quantity. I have recently, in collaboration with Prof. Hugo Erdmann of Halle, made cæsium on a large scale, and it seemed to me advisable to re-determine the specific gravity.

The cæsium for this purpose was purified by several re-distillations in hydrogen, and then examined spectroscopically. The metal was weighed in hydrogen and

then under liquid paraffin, giving the following results as the specific gravity referred to water:—

No. 1.	2.4001
" 2.	2.4004
" 3.	2.3996
" 4.	2.4002
" 5.	2.3998
" 6.	2.4001
Mean.	2.40003

In each case not less than 4 grms. of metal were employed, and the proper correction made for hydrogen weighing.

These results change the atomic volume of cæsium from the figure usually given (70.6) to 55.3, which does not make the drop in the atomic volume curve from cæsium to barium as abrupt as heretofore. It, however, affects the symmetry of the vertical column. The specific gravity of rubidium is probably not correct. I expect to re-determine it shortly.

The following parts of the atomic volume tables illustrate the points in question:—

Table of Atomic Volumes with Sp. Gr. of Cæsium 1.88.

K	45.4	Ca.. .. .	25.4	Sc.. .. .	17
Rb.. .. .	56.2	Sr.. .. .	35	Y	24.8
Cs.. .. .	70.6	Ba	36.5	La	22

Table of Atomic Volumes with Sp. Gr. of Cæsium 2.40003.

K	45.4	Ca.. .. .	25.4	Sc.. .. .	17
Rb.. .. .	56.2	Sr.. .. .	35	Y	24.8
Cs.. .. .	55.3	Ba	36.5	La	22

These experiments confirm Beketoff's results on the atomic volume of cæsium.—*Journal of the American Chemical Society*, xxi., No. 5.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

THIRD PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE AND OXIDE.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

(Continued from p. 113).

II. The Reduction of Cobaltous Oxide.

At this point experimental difficulties in the preparation of the chloride, together with the belief that silica could not be completely removed from the salt without introducing platinum, led to a search for a more satisfactory method. In the hands of the early experimenters upon the atomic weights of nickel and cobalt, reduction of the monoxide yielded good results—results less satisfactory in the case of cobalt than in that of nickel, however, on account of the greater difficulty in preparing the monoxide in a pure state.

Russell (*Journ. Chem. Soc.*, 1863, [2], i., 51), the first investigator to work with cobaltous oxide, found that the higher oxides of cobalt were reduced to the monoxide by heating to a high temperature in air, but that re-oxidation of the monoxide took place while it was cooling. He showed this by igniting in air a crucible containing the black oxide and cooling the crucible suddenly by plunging it into cold water. Under these conditions a film of black oxide was formed on the surface only, while the lower

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxv., No. 3, 1899.

portions remained in the form of brown monoxide. Evidently, to prevent re-oxidation it was only necessary to keep the oxide away from contact with oxygen. The method adopted by Russell was to heat the oxide in a current of inert gas until constant weight was established, and then to reduce the compound in hydrogen, thus obtaining an indirect ratio between oxygen and cobalt.

This method of procedure, which was adopted by all subsequent experimenters on the oxide, seemed open to two serious disadvantages. The first, the difficulty of preparing nitrogen or carbon dioxide free from traces of oxygen, is one which can be surmounted, although not easily. The possibility that small quantities of liberated oxygen may become mechanically entangled in the oxide, in such a way as not to be speedily removed by the current of gas, is a danger even less easily avoided. This oxygen would, of course, re-unite with the monoxide upon cooling, thus making its weight too great.

As an alternative to heating in a current of inert gas, ignition in a vacuum suggested itself as offering distinct advantages, since neither of the dangers just mentioned would be incurred. For this purpose a glazed porcelain tube of 28 m.m. internal diameter, similar to that used for fusing silver in a vacuum, was employed (Richards and Parker, *Proc. Amer. Acad.*, 1896, xxxii., 63; *CHEMICAL NEWS*, lxxv., 173). The tube was closed as usual with Hempel hollow brass stoppers and heated in a perforated Fletcher furnace by means of a large blast lamp, while an ordinary Sprengel air-pump served to exhaust the gases from the tube.

Very pure cobalt, which had been prepared by various methods during the previous work, was converted into the oxide as follows:—From the solution of the metal in pure nitric acid the pink granular cobaltous hydrate was precipitated by adding an excess of pure freshly re-distilled ammonia, and subsequently digesting the mixture upon the steam-bath in a platinum bowl. This precipitate was collected upon a Gooch crucible in which a circular piece of hardened filter-paper was used instead of an asbestos mat. After drying and converting the mass into the black oxide by ignition with an alcohol lamp this material was used directly for analysis. The metal which served as the source of this oxide was known to be free from alkalis and silica (*Proc. Amer. Acad.*, 1897, xxxiii., 120; *CHEMICAL NEWS*, lxxvii., 20), and as neither the nitric acid nor the ammonia could have introduced either of these impurities, the oxide must have been as pure as possible. It has already been shown that specimens of cobalt prepared by any of the methods described in the preceding parts of this paper are essentially identical (*Proc. Amer. Acad.*, 1897, xxxiii., 120; *CHEMICAL NEWS*, lxxvii., 20).

A weighed platinum boat, containing several grms. of cobaltic oxide, was placed in the porcelain tube, and, after the air had been exhausted, the portion of the tube containing the boat was heated to full redness. The expelled oxygen was removed with the air-pump; and the tension of the gases in the tube was finally reduced to a small fraction of a millimetre of mercury. The tube was then cooled while the vacuum was still maintained, air was admitted, and the boat was transferred to the weighing bottle and weighed. Successive ignition for periods of about two hours each reduced the weight of the cobaltous oxide slowly by amounts varying from two- to five-tenths of a m.grm., until constant weight within one-tenth of a m.grm. was obtained. During this process the cobaltous oxide, which was light brown at first, gradually assumed a darker tint.

Since complete reduction of this oxide by hydrogen at a temperature which could be borne by hard glass is very slow, the reduction was conducted in a porcelain tube heated by the furnace. The metallic cobalt, which sintered together in such a fashion as to occupy not more than one-fifth the original volume of the oxide, was cooled in a vacuum, and then transferred to the weighing bottle and weighed. Constant weight was obtained without difficulty. (Sintered cobalt does not occlude important

amounts of hydrogen, even when cooled in this gas; a paper showing this fact will soon be published).

In the following table are given the results obtained by this method of procedure. The correction to a vacuum standard of +0.000069 grm. per grm. of cobaltous oxide was applied, the specific gravity of the oxide being taken as 5.68 (Joule and Playfair, "Landolt and Börnstein's Tabellen," 1894, p. 134). O = 16.000.

Number of analysis.	Weight of cobaltous oxide in vacuum. Grms.	Weight of cobalt in vacuum. Grms.	Atomic weight of cobalt.
1.	7.04053	5.53779	58.962
2.	6.69104	5.26312	58.974
3.	7.83211	6.15963	58.927
			58.954

From the fact that the above results agree neither among themselves nor with the results obtained from the bromide (58.995), it seemed highly probable that all excess of oxygen had not been removed from the cobaltous oxide. It has been shown that oxides made by ignition of nitrates give off their extra "included" oxygen only upon long continued heating, the gas gradually working its way out by a process of dissociation and re-combination (T. W. Richards, *Proc. Amer. Acad.*, xxxiii., 399; *CHEMICAL NEWS*, lxxix., 19). Here also the oxygen combined with the innermost parts of the monoxide, too tightly enclosed to escape easily, must have required time to force its way out by the same process.

Accordingly, in the next analysis the oxide was heated for much longer periods in the highest vacuum obtainable. Under these conditions the loss of weight between each two ignitions increased very materially, amounting to more than a m.grm. in each case, and culminated in a loss of 3 m.grms. accompanied by a decided darkening of the oxide. This called to mind an experiment made by Dr. Cushman in his work upon the atomic weight of nickel (*Proc. Amer. Acad.*, xxxiii., 424; *CHEMICAL NEWS*, lxxvi., 284). In this experiment he ignited nickelous oxide to bright redness in a current of nitrogen. Upon removal from the ignition tube the oxide was found to have been partially converted into metallic nickel, owing doubtless to the dissociation of the oxide into metal and oxygen, and the subsequent carrying away of the oxygen by the current of nitrogen. Cupric oxide, when heated only to 700–800°, is known to dissociate perceptibly into cuprous oxide and oxygen (*Proc. Amer. Acad.*, xxxiii., 421). As a matter of fact, when the cobaltous oxide was removed from the boat, it was found to have been reduced to such an extent that enough metallic cobalt had been formed to alloy with the platinum; thus cobaltous oxide also, at about 800°, dissociates very considerably into cobalt and oxygen. In the zeal to obviate oxidation, the opposite error had been encountered. Obviously the only method of obtaining the monoxide free from the metal was to determine the tension of the oxygen evolved from it at the temperature to which the oxide was heated, and always to keep the tension above this point during the ignition.

In the earlier experiments, an exceedingly slight known leakage of water through the brass stoppers into the tube may explain why the reduction of the monoxide did not occur, for metallic cobalt decomposes water at a high temperature.

Some of the brown monoxide which had suffered partial reduction in the experiment described above, and which consequently must have been free from higher oxides, was now heated in a hard glass tube sealed at one end; and the tube was exhausted to within two-tenths of a millimetre of mercury by means of the Sprengel pump. When the pump was stopped the tension of the gas slowly increased from four-tenths of a millimetre at 400° to one and five tenths m.m. at full redness, the highest temperature obtainable with the Bunsen lamp. The pressure of the

oxygen resulting from the dissociation of the black oxide of cobalt was determined to be in the neighbourhood of 630 m.m. at the same temperature. Evidently, if the tension of the oxygen remains below 630 m.m. of mercury, the higher oxides of cobalt cannot exist (except in an imprisoned state); and, on the other hand, if the tension of the oxygen does not fall below one and five tenths m.m. there can be no reduction of the monoxide. In the next analysis the oxygen was removed from the tube as fast as it was evolved until the tension of the gas remaining was about one and five tenths m.m. The pressure inside the tube was kept at this point until heating ceased, when the tube was exhausted as completely as possible. In subsequent ignitions of this boat-load the tube necessarily contained air, not oxygen, and allowance was made for this fact by increasing the pressure five times. In this case also constant weight was obtained only after many ignitions although the differences in the weight of the oxide were small. 7.74242 grms. (in vacuum) of cobaltous oxide yielded 6.09219 grms. of cobalt, corresponding to an atomic weight of 59.068.

Evidently even here traces of metal had been found during the heating of the monoxide. This undesired reduction could have taken place only during the cooling, for at all other times the tension of the oxygen was greater than the dissociation pressure of the monoxide. Measures were then taken to make this error impossible.

On account of the size of both tube and furnace, the cooling was necessarily very slow; this fact is indeed an advantage, because otherwise the life of a tube would be short. Assuming that the tube cooled always at the same rate, the tension of the oxygen from the dissociated oxide after any given interval of time from the cessation of ignition should always be the same. A table embodying such tensions was prepared by repeatedly exhausting the tube to a tension slightly below the supposed point, and allowing the pressure inside the tube to reach a maximum. This table, which was obtained by averaging three different series of observations, is given below. The readings were obtained by means of a McLeod gauge:—

Time from cessation of ignition.	Tension of oxygen resulting from dissociation.
Minutes.	M.m.
15	0.80
30	0.56
45	0.28
60	0.21
75	0.11
90	0.07

These values have no meaning except for the particular process by which they were obtained, but they show plainly how great a chance for error existed when the tube was exhausted completely as soon as ignition ceased.

In the next analysis the procedure was exactly similar to that in analysis 4, except that during cooling the values indicated in the table were maintained. No essential loss of weight took place after the third heating, although several additional ignitions were carried out for the sake of certainty. 10.58678 grms. (in vacuum) of cobaltous oxide yielded 8.32611 grms. of cobalt, corresponding to an atomic weight 58.929.

In the face of this unsatisfactory result, there seemed nothing further to do except to attempt the detection of the presence of impurities. Three possibilities were open: the oxide might contain moisture, enough nitrate might have been carried down by the cobaltous hydrate to cause a small amount of nitrogen and oxygen to be occluded by the oxide, or else some higher oxide of cobalt might be present.

It was easily shown that cobaltous oxide is as a matter of fact slightly hygroscopic. Several grms. exposed for twenty-four hours to an atmosphere saturated with moisture gained 5 m.grms. in weight, most of which was lost in a short time in a desiccator. It was satisfactorily proved, however, by suitable experiments which need not be re-

counted, that not enough moisture could have crept in during any of the processes used to cause any important error.

In order to prove the absence of included gases, a specimen of oxide which had been treated in the same manner as the material used in analysis 5 was dissolved in hydrochloric acid in an apparatus for measuring the gases evolved during the solution (*Proc. Amer. Acad.*, xxxiii., 403, and *Journ. Chem. Soc. Trans.*, lxxi., 559). No gas was given off; but upon treating the solution with potassic iodide and starch, an unmistakable liberation of iodine was detected. This showed conclusively that some higher oxide of cobalt had remained undecomposed, for pure cobaltous chloride has no immediate effect on hydriodic acid. The presence of the imprisoned higher oxide is undoubtedly the reason for the low value for the atomic weight of cobalt obtained in this way.

The cobalt itself obtained from the pure oxide by reduction at a high temperature is very permanent in the air, and occludes only traces of hydrogen.

With great reluctance the work upon the monoxide was abandoned at this point; for a substance whose composition varies so widely under conditions which vary so slightly is obviously unfitted for work of the highest accuracy. As in the case of cobaltous bromide, the preparation of this substance even in a reasonably pure state appears to be an impossibility. Unfortunately the accurate estimation of the worst impurity in this case, cobaltic oxide, is a very difficult matter. An attempt to use pure cobaltic oxide itself as the basis of the determination proved to be equally unsatisfactory.

The results of this part of the investigation are nevertheless of considerable import in the light they throw upon previous analyses of the monoxides of both nickel and cobalt as well as upon the accuracy of the results obtained in the analyses of cobaltous halides described in this paper. The material which gave the lowest result contained oxides of cobalt higher than the monoxide, hence these results are too low. On the other hand, the material which gave the highest result was heated under conditions which theoretically should have caused, and evidently did cause, partial reduction of the oxide to metal. The true value of the atomic weight of cobalt must lie between these two extremes, 58.93 and 59.07; and until trustworthy evidence to the contrary has been produced, the most probable value seems to be the mean 58.995, obtained from the analysis of the bromide.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 1st, 1900.

Professor THORPE, F.R.S., President, in the Chair.

MR. J. W. ANDERSON was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Henry Jennings, Marlowes, Hemel Hempstead, Herts; Robert Pettigrew, 50, Cresswell Grove, West Didsbury, Manchester; Geoffrey Surtees Phillpotts, 82, James's Street, Dublin.

Of the following papers, those marked * were read:—

*29. "On Pilocarpine and the Alkaloids of *Jaborandi Leaves*." By H. A. D. JOWETT, D.Sc.

On account of the doubts expressed by Kundsén, Merck, and others, as to the reliability of the work of Hardy and Calmels on this subject, and the recent conflicting statements of Petit and Polonowski and of Merck, the author has undertaken a complete study of these

alkaloids. The present paper deals with the characterisation of pilocarpine, isopilocarpine (pilocarpidine of Petit and Polonowsky), pilocarpidine and jaborine, with a few preliminary experiments on the constitution of the alkaloid. The results, which are given in detail in the paper, may be briefly summarised as follows:—

1. The original papers of Hardy and Calmels are very unsatisfactory, as they contain neither physical constants, nor analyses of the products described. In most cases the author is unable to confirm their result. On the other hand, a satisfactory explanation is afforded of the apparent contradiction between the work of Petit and Polonowsky and that of Merck.

2. The physical constants and description of the salts of pilocarpine, as given by Petit and Polonowsky, are generally confirmed, though in several cases there are slight differences, due probably to the use of purer material by the author.

3. The acid character of pilocarpine has been investigated and the previous work of Hardy and Calmels on this subject corrected.

4. The existence of a base, isomeric with pilocarpine, and produced from it by the action of heat or alkali, as previously stated by Petit and Polonowsky, is confirmed. As this base is isomeric with and bears a close relation to pilocarpine, it is proposed to call it isopilocarpine, as the term pilocarpidine, previously used for it, must be retained for the product previously described by Harnack under this name. It is shown that isopilocarpine can be distilled unchanged in a vacuum.

5. Some of the physical constants of isopilocarpine and its salts as given by Petit and Polonowsky are confirmed, and others corrected.

6. Proof is given of the existence of isopilocarpine in *jaborandi* leaves, and in the pilocarpine nitrate of commerce.

7. The existence of the pilocarpidine of Harnack and Merck, and their statements regarding its composition, are confirmed. Some of the salts of the base are described.

8. The absence of pilocarpidine in the pilocarpine nitrate of commerce, and in the varieties of *jaborandi* leaves at present in the market, is proved.

9. The jaborine of commerce is shown to be a mixture of isopilocarpine, pilocarpidine, and a trace of pilocarpine with colouring matter. No evidence has been obtained of the existence of an alkaloid with the properties of jaborine, or of any other than those described in this paper.

10. Several experiments on the constitution of pilocarpine have been repeated, and the results of Hardy and Calmels corrected.

Further experiments on this subject are in progress.

The author has been unable to obtain any evidence confirmatory of the constitutional formula which was proposed by Hardy and Calmels and widely adopted.

DISCUSSION.

Mr. KINGZETT referred to his work on pilocarpine, which was communicated to the Society in 1876. He then proposed for this alkaloid the formula $C_{23}H_{35}N_4O_4$, and, although this formula had been modified by later workers to $C_{11}H_{16}N_2O_2$, which was also adopted by Dr. Jowett, he still adhered to the formula he had originally suggested, because it was based on several concordant analytical results.

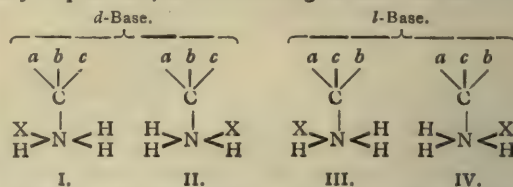
Professor DUNSTAN said that our knowledge of the chemistry of pilocarpine and the alkaloids of *jaborandi* was in a very uncertain state, and he was glad to find that Dr. Jowett had commenced its careful revision. The alleged existence of jaborine, an alkaloid antagonistic to pilocarpine, had long been a difficulty in the medicinal employment of this drug. Dr. Jowett appeared to have shown good grounds for the conclusion that no such alkaloid as jaborine exists in the plant, and he had made a serious criticism of the generally accepted results and conclusions of Hardy and Calmels.

*30. "Isomeric partially Racemic Salts containing Quinquevalent Nitrogen. Hydrindamine Bromocamphorsulphonates, Chlorocamphorsulphonates, and cis- π -camphanates." By F. STANLEY KIPPING, Ph.D., D.Sc., F.R.S.

On continuing the investigation of the isomeric hydrindamine bromocamphorsulphonates already briefly described (*Proc.*, 1899, xv., 172), it has been found that both compounds, when decomposed by barium hydroxide, yield a base identical with externally compensated hydrindamine. It is proved that the optical inactivity of the base is not due to racemisation having occurred,—hence the formation of the two bromocamphorsulphonates cannot be attributed to a re-solution of the base into its enantiomorphous components. As to the possibility of the existence of two isomeric forms of bromocamphorsulphonic acid, it is shown that the acid in each salt is the same. Hence it is concluded that the isomeric hydrindamine bromocamphorsulphonates are both partially racemic salts.

The specific rotations of these salts are different in alcoholic solutions of equal concentration; their specific rotations in 1 percent aqueous solutions are, for the more sparingly soluble α -salt $[\alpha]_D = +60^\circ$, and for the β -salt $[\alpha]_D = +49.7^\circ$, hence the molecular rotations are $[M]_D = +266.5^\circ$ and $[M]_D = +220.5^\circ$ respectively. As the molecular rotation of bromocamphorsulphonic acid, calculated from the determinations of Walden (*Zeit. Phys. Chem.*, 1894, xv., 196), and from data given in the paper is $+270^\circ$, the low molecular rotation of the β -salt might be taken to indicate either the existence of an isomeric form of bromocamphorsulphonic acid or the presence of levorotatory hydrindamine. It is shown that as the salt in question is composed of *d*-hydrindamine α -bromocamphorsulphonate and *l*-hydrindamine α -bromocamphorsulphonate, which salts have probably widely different specific rotations in a non-dissociated condition, the apparently abnormal molecular rotation of the β -salt may be attributed to incomplete ionic dissociation.

The following is the explanation of this form of isomerism suggested by the author; it is equally applicable to all the other cases of isomerism of this kind which he has observed. When an externally compensated base combines with an optically active acid, four different salts may be produced, as the following formulæ indicate:—



Of these four compounds, no two are mirror images, but as the relation between I. and IV. on the one hand, and II. and III. on the other, would probably be that of mirror images if the group X were not enantiomorphous, it may be presumed that I. and IV. would be formed in equal quantities, and might unite to form a partially racemic salt; the isomeric partially racemic salt would be similarly produced from II. and III.

Externally compensated hydrindamine unites with chlorocamphorsulphonic acid to form unequal quantities of two salts which are isomeric when anhydrous, but which are usually differently hydrated. The more sparingly soluble α -salt, which is produced in by far the larger quantity, crystallises from water in opaque, very slender prisms, whereas the β -isomeride is usually deposited in more transparent and compact prisms.

The relationship between these two salts is analogous to that of the compounds above described, but the β salt differs from the corresponding salt of the bromo-acid, as it exists in two differently hydrated forms, one of which is indistinguishable in appearance from the α -salt. The conditions which determine the formation of one or other variety of the β -salt are not yet known with certainty.

The α - and β -compounds are both partially racemic salts which are not convertible the one into the other by ordinary solvents, but by repeatedly evaporating a solution of the β -salt with externally-compensated hydrindamine, the α -isomeride is obtained.

The specific rotations of the isomerides in alcoholic solution are practically identical, but when dissolved in water, and especially in chloroform, different values are obtained. Determinations in approximately 1 per cent aqueous solutions gave the following average results:—For the α -salt $[\alpha]_D = +47^\circ$, $[M]_D = +188^\circ$; for the β -salt $[\alpha] = +50.5^\circ$, $[M]_D = +202^\circ$.

The molecular rotation of chlorocamphorsulphonic acid was found to be $[M]_D = +189^\circ$, so that the molecular rotations of the partially racemic salts are practically identical with the values they might be expected to give under the above conditions. The two differently hydrated forms of the β -salt were found to have the same specific rotation when calculated for the anhydrous salt.

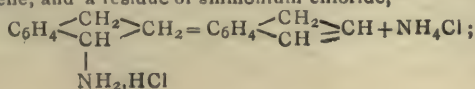
When externally compensated hydrindamine is neutralised with *cis*- π -camphanic acid, unequal quantities of two isomeric anhydrous salts are obtained. The more sparingly soluble α compound melts at about 192° , the isomeric β -salt at about 172° ; when crystallised from water or other solvents, both salts are deposited in very slender prisms practically identical in appearance. The base liberated from either of these salts by barium hydroxide is optically inactive, and as each salt, when directly decomposed by strong hydrochloric acid, gives optically inactive hydrindamine hydrochloride, it is clear that the two salts do not correspond with the two enantiomorphous hydrindamines, but that both are partially racemic substances.

The β -salt may be converted into the α -form by evaporating its aqueous solution with externally compensated hydrindamine, which seems to indicate that the relation between these two salts is similar to that between the isomeric salts of chloro- and bromo-camphorsulphonic acids from which they differ in undergoing hydrolytic dissociation, and this leads to other differences in behaviour, such as the conversion of the one salt into the other in aqueous, and apparently also in alcoholic solution, rendering their separation and the determination of their properties a matter of some difficulty.

Determinations of the specific rotations of these salts in solution in methyl alcohol showed wide variations; different preparations of the α -salt, all melting at the same temperature, gave values for $[\alpha]_D$ varying from -2° to $+20^\circ$, and in the case of β -salt from -6° to -10° . By repeated fractional crystallisation, these values were considerably raised, the greatest rotation for the α -salt being $[\alpha]_D = +24^\circ$, and for the β -salt $[\alpha]_D = -20^\circ$.

In solution in methyl alcohol, the rotation of the α -salt is very low at first, being $[\alpha]_D = +5^\circ$ a few minutes after solution; after forty-five minutes, it rises to $[\alpha]_D = 24^\circ$, at which it seems to remain constant. The cause of this change is not clear, as the β -salt, in other respects so similar, does not show it. In dilute aqueous solutions, both salts have practically the same rotation, $[\alpha]_D = -16^\circ$, and the molecular rotation calculated from determinations in 1 per cent aqueous solutions is $[M]_D = -53^\circ$ approximately, a value agreeing fairly well with that obtained for *cis*- π -camphanic acid from an examination of its piperidine salt and of its solution in dilute aqueous ammonia.

*31. "New Syntheses of Indene." By F. STANLEY KIPPING, Ph.D., D.Sc., F.R.S., and HAROLD HALL, A.I.C. In the course of some work connected with α -hydrindamine, it was found that the hydrochloride of this base is readily decomposed when heated, giving a distillate of indene, and a residue of ammonium chloride,—



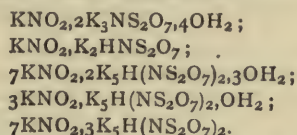
the reaction seems to take place almost quantitatively, and affords the most convenient method yet known for the preparation of this unsaturated hydrocarbon. Trimethylhydrindamine iodide undergoes a similar decomposition when it is heated, yielding indene and trimethylamine hydriodide. The indene obtained by either of these methods is identical with the hydrocarbon isolated from coal-tar by Krämer and Spiker, and also with that obtained by Perkin and Reváy by the distillation of hydrindene-carboxylic acid (*Trans.*, 1894, lvi., 228). The identity of all three preparations was established, the differences between synthetical and coal-tar indene observed by Perkin and Reváy (*loc. cit.*) being doubtless due to the presence in the latter of impurities which they were unable to remove.

Trimethylhydrindamine iodide, $\text{C}_9\text{H}_9\text{N}(\text{CH}_3)_3\text{I}$, is obtained when hydrindamine is treated with methyl iodide at ordinary temperatures; it crystallises well, is dimorphous, and melts at about 190° .

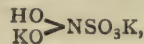
It seems probable that the reactions described above will also occur in the case of the hydrochlorides of other aromatic partially reduced bases, and experiments will be made to test this.

*32 "Potassium Nitrito-hydroximidosulphates and the Non-existence of Dihydroxylamine Derivatives." By E. DIVERS and T. HAGA.

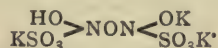
Potassium nitrite forms crystalline compounds with the normal, the $2/3$ normal, and the $5/6$ normal potassium hydroximidosulphates, all readily decomposed by solution in water, but re-crystallisable from sufficiently concentrated solutions of potassium nitrite or of this salt and some potassium hydroxide. Their formulæ are—



The discovery of these salts has enabled the authors to destroy what little evidence there was for the existence of dihydroxylamine compounds, two of which have been described by Raschig. One of these he treats as being dipotassium monosulphonated dihydroxylamine,—



and the other, more easily obtained, as the anhydro-compound of this with potassium monosulphonated dihydroxylamine,—



The authors have followed Raschig's methods pretty closely and with a sufficient degree of success, and have found his preparations indistinguishable from synthetically prepared compounds, somewhat impure, of nitrite with the $5/6$ normal hydroximidosulphate, and the $2/3$ normal hydroximidosulphate respectively. According to them, the anhydro- 'dihydroxylamine' compound was $\text{KNO}_2, \text{K}_2\text{HNS}_2\text{O}_7$, whilst the other was impure $3\text{KNO}_2, \text{K}_5\text{H}(\text{NS}_2\text{O}_7)_2, \text{OH}_2$. Two other salts prepared by Raschig, which have figured respectively as an isomeride of Pelouze's hyponitrosulphate and as an isomeride of the $5/6$ normal hydroximidosulphate, are considered by the authors to be also only impure nitrito-hydroximidosulphates.

*33. "Identification and Constitution of Fremy's 'Sulphazotised Salts of Potassium.'" By E. DIVERS and T. HAGA.

By treating a solution of potassium nitrite and hydroxide with sulphur dioxide, Fremy in 1845 obtained a series of salts, and by their hydrolysis or oxidation, other salts, all sulphonated derivatives of nitrous acid. The constitution of several of these has remained undetermined; attempts to reproduce some of them have

failed to such an extent as to make even their existence doubtful. The authors have been fairly successful in obtaining Fremy's results, and with the help of the knowledge summarised in the preceding abstract, are able to express the constitution of his salts with confidence. His *sulphazate*, which neither Claus nor Raschig succeeded in obtaining, was made without difficulty by following Fremy's directions. It is the potassium nitrito-2/3-normal hydroximidodisulphate partly converted, by treatment with alkali, into the normal hydroximidodisulphate. His *sulphazite* is the nitrito-5/6-normal hydroximidodisulphate of which the formula is given in the preceding abstract. His *metasulphazate* is described as a jelly, which on pressure in a cloth became wax-like. The authors have obtained a salt in fine, silky fibres in all other respects apparently identical with that of Fremy, and this proved to be potassium nitrito-normal hydroximidodisulphate, mixed with a little normal hydroximidodisulphate. His *metasulphazotate*, as obtained by the authors, proved to be the potassium nitrito-2/3-normal hydroximidodisulphate, mixed or combined with a little normal hydroximidodisulphate. The constitution of Fremy's *basic* and *neutral sulphazotates*, *sulphazidate*, *sulphammonate*, and *sulphamidate* have been already determined, whilst his *sulphazilate* and *metasulphazilate* appear to have the formulæ $\text{ON}:(\text{SO}_3\text{K})_2$ and $\text{ON}:(\text{SO}_3\text{K})_3$.

(To be continued).

PHYSICAL SOCIETY.

Special Meeting, March 9th, 1900.

Prof. EVERETT, F.R.S., Vice-President, in the Chair.

A PAPER ON "*The Damping of Galvanometer Needles*" was read by Mr. M. SOLOMON.

The solution of the equation of motion for a magnetic needle, swinging in a uniform magnetic field, points to the conclusion that the ratio of the period to the logarithmic decrement is independent of either the moment of the needle or the strength of the controlling field, and is simply a function of the damping coefficient, and the moment of inertia of the moving system. This ratio should therefore be constant if these latter quantities are constant. Experiments to test the constancy of period to logarithmic decrement have been conducted at the Central Technical College at various times since 1891, and they have invariably pointed to a variation in the value of the ratio. The object of the present paper is to discover the cause of this variation. It may be due to an alteration in the moment of inertia or to an alteration in the damping coefficient. If the control magnets are either directly above or directly below the needle there is no chance of any change in the moment of inertia. The damping coefficient depends on three things:—(1) viscosity of the air, (2) viscosity of the suspension, and (3) eddy currents. The author has carried out experiments with a galvanometer on open circuit and finds a constant value for the ratio; the viscosity of the air and suspension therefore cause no variation. Upon closing the circuit and repeating the experiments the value of period over logarithmic decrement alters. The variation is therefore due to eddy currents. The damping factor due to eddy currents may vary owing to three causes:—(1) change in moment of needle due to change in field strength, (2) effects of self-induction, (3) effects of rise of temperature on the resistance of the coils. The author points out that the two latter causes would tend to alter the ratio in the wrong direction, and he therefore concludes that the variation is due to an alteration in the strength of the swinging needle, produced by altering the strength of the controlling field.

Mr. BLAKESLEY said it was interesting to note the fact that the ratio of period to decrement was independent of the controlling field. In the case of a condenser dis-

charging this ratio is independent of the capacity, in the case of a tuning fork, of the rigidity and in the case of water oscillating up and down in a U-tube, of the acceleration due to gravity.

Mr. ROSENBAUM said that the ratio considered was constant in the case of a Nalder D'Arsonval galvanometer.

Mr. SOLOMON said that his arguments did not apply to galvanometers of this description because the swinging system was not a magnetic needle, but simply a coil.

A paper on "*The Distribution of a Gas in an Electric Field*" was read by Mr. G. W. WALKER.

The author has considered a gas as consisting of a number of molecules, each containing two atoms of equal mass, one positively and the other negatively charged with electricity. When under the action of electrical forces some of the molecules split up, and we arrive eventually at a steady state in which there is a definite number of undissociated molecules and of free positive and free negative atoms. Treating the problem as one-dimensional, the potential at any point is expressed in general by elliptic functions, and is therefore periodic. Applying the results to the case of a vacuum-tube it is found that there is superimposed upon the gradual fall of potential along the tube, minor periodic variations which it is suggested are connected with the striæ of discharge. Both the matter density and the electric density are periodic along the tube. If the places of maximum matter density coincide with the places of minimum electrical action, then whether luminosity is due to collisions or recombinations there will be maximum luminosity at these points. In general, these points do not coincide, and thus the positions of maximum luminosity are not clearly defined. The analysis leads to the conclusion that the distance between the striæ is inversely proportional to the density of the gas and to the current strength, and these facts have been experimentally verified.

Mr. C. E. S. PHILLIPS exhibited a "*Surface Tension Lecture Experiment*."

The effects of surface tensions were exhibited by placing water between two pieces of microscope cover glass. When the glasses are circular they set in any position, and one can be made to rotate upon the other. If the plates are square or elliptical they set in a definite position, to which they immediately return if displaced. Mr. Phillips pointed out how two circular discs with liquid between could be used from which to suspend the moving system of a galvanometer.

Mr. COCHRANE suggested the use of some liquid which would evaporate less quickly than water.

Mr. BLAKESLEY asked what accuracy could be obtained with such an arrangement, and what weight it would be possible to support without squeezing out the water.

The meeting then adjourned until March 23rd.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 8, February 19, 1900.

Researches on the Isomerism of Sulpho-cyanic Derivatives.—M. Berthelot.—This paper is unsuitable for abstraction.

Method of Preparation of Arsenides, Alkaline Stibnides, and some Alloys of the Alkaline Metals.—P. Lebeau.—Arsenic or either gaseous or liquefied arseniuretted hydrogen react on the alkaline metals, but do not give pure crystallised arsenides. Liquid arseniuretted hydrogen does not dissolve the alkaline

metals either at -80° or at the ordinary temperature and pressure. Arsenium metals comparable with the ammonium metals are not formed. The employment of an alkaline metal as solvent of its arsenide, and the elimination of excess of metal by means of liquefied ammonia gas, constitutes an excellent method of preparing crystalline arsenides. This method admits of general use, and allows of the preparation of definite crystalline alloys of the alkaline metals.

Nitrogen Iodide.—C. Hugot.—The author obtains the bodies $\text{NI}_3 \cdot 3\text{NH}_3$, $\text{NI}_3 \cdot 2\text{NH}_3$, and $\text{NI}_3 \cdot \text{NH}_3$ in a well crystalline form. These can be considered merely as ammoniacal combinations of nitrogen iodide, on account of the facility with which they lose their ammonia. These substances are prepared by the action of liquid ammonia gas on nitrogen iodide under varying experimental conditions.

Meconine, Opianic Acid, and Hemipinic Acid.—Emile Leroy.—The author determines the heat of formation and combustion of these substances, and obtains the following numbers:—*Meconine*, $\text{C}_{10}\text{H}_{10}\text{O}_4$.—

Heat of combustion at constant volume and pressure 1090.4 cal.
Heat of formation from its elements +197.7 "

Opianic Acid—

Heat of combustion at constant volume .. 1260.7 cal.
" " " pressure .. 1261.0 "
" formation from its elements +190.4 "

Hemipinic acid, $\text{C}_{10}\text{H}_{10}\text{O}_6$, an acid resulting from the oxidation of opianic acid.

Heat of combustion at constant volume .. 1024.9 cal.
" " " pressure .. 1024.6 "
" formation from its elements +263.5 "

Rapid Method of Estimating Carbonic Acid in Various Gases.—Léo Vignon and Louis Meunier.—Into the flask containing carbonic acid mixed with other neutral gases little by little a solution of lime-water of known strength, reddened with phenolphthalein, is introduced. The lime-water only retains its rose colour after complete saturation with carbonic acid. The operation is rendered more rapid and more complete by adding a little ethyl alcohol; this substance facilitates the formation of insoluble calcium carbonate. The proportion of carbonic acid present is measured by the quantity of lime-water used to obtain the red colouration, a deduction being made for the quantity absorbed to allow of the colouration of the phenolphthalein. This method can be used to estimate the CO_2 in furnace gases, &c.

Volumetric Estimation of Boric Acid.—Alfred Stock.—Whilst trying to analyse a certain number of borides, the author employed Jones's method, by which, in an acid solution of boric acid, the mineral acids are neutralised by a mixture of iodide and iodate of potassium, which has no action on the boric acid. The author finds the method not satisfactory, and introduces various improvements:—(1) It is essential to avoid even minute traces of carbonic acid; this end can only be attained by boiling all the reagents to eliminate the last traces of CO_2 . (2) Although the metals of the alkalis and alkaline earths do not affect the titration of boric acid, other metals, whose solutions are precipitated by soda, cause interference, and have to be carefully eliminated from the solution before titration of the boric acid.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., Nos. 20-21.

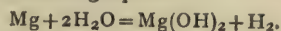
Analysis of some Commercial Samples of Carbide of Calcium.—Henri Moissan.—Already inserted.

The Preparation of Crystallised Calcium.—Henri Moissan.—Already inserted.

Preparation and Properties of Hydride of Calcium.—Henri Moissan.—Pure crystallised calcium is placed in a nickel boat in a glass tube traversed by a current of pure dry hydrogen. On raising the temperature of the calcium to a dull red, it takes fire in the atmosphere of hydrogen. The gas is rapidly absorbed, and a white substance is formed, which is hydride of calcium. This hydride is stable at a high temperature, and is an energetic reducing agent; its formula is CaH_2 . On contact with water it decomposes with violence. In this compound the hydrogen is comparable with the metalloids (carbon or phosphorus), and not with the metals. There are in reality two series of hydrides, in one of which the hydrogen seems to be in solution in the metals; and the others forming at a more or less elevated temperature, having all the characteristics of definite chemical compounds.

Preparation and Properties of Nitride of Calcium.—Henri Moissan.—When a morsel of pure crystallised calcium is placed in an atmosphere of pure dry nitrogen, no change takes place in the cold, but on raising the temperature there is at first a slow absorption of gas and a change of colour in the metal, which gradually becomes yellow, then bronze. On further increasing the temperature the colour deepens, and at a dull red heat the combination takes place with incandescence. When the reaction takes place at about 1200° the compound obtained is crystalline; it answers to the formula N_2Ca_3 . It reacts readily with chlorine, bromine, iodine, oxygen, sulphur, and phosphorus, and is destroyed by carbon at a high temperature. With anhydrous alcohol it gives ammonia and ethylate of calcium. It also decomposes on contact with cold water, giving off ammonia.

The Action of Magnesium on Saline Solutions.—D. Tommasi.—When magnesium is treated with a solution of chloride of potassium, hydrogen is given off, the liquid becomes cloudy, and acquires a slightly alkaline reaction. The product of this reaction is hydrate of magnesium. The chloride of potassium is not decomposed by this reaction, but plays no other part beyond helping the oxidation of the magnesium. The reaction thus only takes place between the water and the magnesium, according to the following equation:—



The author then gives a list of chlorides and sulphates of a number of metals, and the action their solutions have on metallic magnesium.

Fluorine in the Mineral Waters of Portugal.—A. J. Ferreira da Silva and Alberto d'Aguiar.—Already inserted in full (see vol. lxxxi., p. 4).

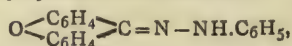
MISCELLANEOUS

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th instant, His Grace the Duke of Northumberland, K.G., President, in the Chair. Mrs. Colenso, Miss A. C. Colthurst, Professor J. D. Everett, Professor P. F. Frankland, Mr. A. C. Ionides, Mrs. A. B. Kempe, Mr. A. G. Low, Colonel W. T. Makins, Colonel F. Rhodes, Mr. W. M. Still, Major F. Trench-Gascoigne, Dr S. West, Mrs. West, and Miss H. M. White, were elected Members of the Royal Institution.

On the Oxime and the Phenylhydrazone of Xanthone.—C. Graebe and P. Roeder.—Meyer and Spiegler, basing their ideas on the fact that xanthone and euanthone do not give any products of condensation either with hydroxylamine or phenylhydrazine, came to the conclusion that the compounds of the euanthone group were lactones. Graebe and Feer have, however, furnished the proof that xanthone ought to be considered

as a cyclic ketone, and its formation by means of phenylsalicylic acid has confirmed this view. In fact, the authors have succeeded in preparing the phenylhydrazones of xanthone by means of its thio-derivative $O < \text{C}_6\text{H}_4 > \text{CS}$, to which they give the name xanthione.

This compound was itself prepared from xanthone-phenylimine, obtained by heating a mixture of equal parts of aniline and 2.2'-dioxymbenzophenone for two or three hours, at 200°. Xanthone-phenylimine, dissolved in alcohol and saturated with H_2S , gives xanthione which occurs in the form of long needles possessing dichroism to a strong degree, and melting at 156°. Concentrated H_2SO_4 dissolves it with a yellow colour with green phosphorescence. Xanthione, heated in alcoholic solution with hydrochlorate of hydroxylamine and carbonate of sodium, gives the corresponding oxime, the xanthone oxime, $O < \text{C}_6\text{H}_4 > \text{C}=\text{N.OH}$, which concentrated sulphuric acid dissolves yellow, with blue phosphorescence, and which melts at 161°. Xanthione, heated for four or five hours in alcoholic solution with excess of phenylhydrazine, gives the phenylhydrazone of xanthone,—



which crystallises in alcohol in golden-yellow needles fusible at 152°.—*Berichte*, vol. xxxii., p. 1688.

MEETINGS FOR THE WEEK.

- MONDAY, 19th.—Society of Arts, 8. (Cantor Lectures). "Photography of Colour," by E. Sanger Shepherd.
TUESDAY, 20th.—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
WEDNESDAY, 21st.—Society of Arts, 8. "The Use and Abuse of Food Preservatives," by Dr. Samuel Rideal.
— Microscopical, 7.30. Exhibition of Slides of New, Rare, and Foreign Rotifera, by C. F. Rousselet, Curator R.M.S.
THURSDAY, 22nd.—Royal Institution, 3. "Equatorial East Africa and Mount Kenya," by H. J. Mackinder, M.A.
FRIDAY, 23rd.—Physical, 5. "An Electro-magnetic Experiment," by Prof. S. P. Thompson, F.R.S. "Some Experiments illustrating Syntony" and "An Electrical Micrometer," by P. E. Shaw.
— Royal Institution, 9. "Some Modern Explosives," by Sir Andrew Noble, K.C.B., F.R.S., M.Inst.C.E.
SATURDAY, 24th.—Royal Institution, 3. "Polarised Light," by The Rt. Hon. Lord Rayleigh, M.A., D.C.L., &c.

NOW READY.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2104.

ON THE SPECIFIC HEAT OF METALS AND THE RELATION OF SPECIFIC HEAT TO ATOMIC WEIGHT.*

By W. A. TILDEN, D.Sc., F.R.S.,
Professor of Chemistry in the Royal College of Science, London.

WITH AN APPENDIX BY PROFESSOR JOHN PERRY, F.R.S.

THE experiments described in this paper were begun with the object of assisting in the determination of the relative values of the atomic weights of cobalt and nickel, but were continued with the further purpose of testing the validity of the law of Dulong and Petit.

The metals cobalt and nickel closely resemble each other in density, melting-point, and other physical properties, as well as in atomic weight. The pure metals were prepared for the purposes of these experiments with the most scrupulous care, the cobalt by taking advantage of the slight solubility of purpleo-cobaltamine hydrochloride in strongly acid solutions, and the nickel by deposition from the carbonyl compound and subsequent solution of the metal and electro-deposition. Both were fused by means of an oxyhydrogen flame, and afterwards shaped into bars. For the estimations of specific heat between 15° C. and 100° C. the differential steam calorimeter of Professor Joly was employed.

The mean specific heat of cobalt within these limits of temperature was found to be 0.10303.

The mean specific heat of nickel was found to be 0.10842.

In order further to test the method and the conclusion from the case of cobalt and nickel, gold was compared with platinum, and copper with iron.

The following are the mean specific heats for these pure metals after fusion, and within the same limits of temperature:—

Gold	0.03035
Platinum	0.03147
Copper	0.09232
Iron	0.10983

When these values for the specific heats are multiplied by the respective atomic weights of the several metals, the products are not constant, as the law of Dulong and Petit would seem to require if applicable at all temperatures.

The influence of impurities on the specific heat of several metals was then investigated and a number of results are given, from which it appears that small quantities of carbon or other non-metallic element tend to increase the specific heat appreciably, while the presence of a small quantity of a foreign metal seem to produce little effect.

A series of calorimetric experiments were next made by the method of mixtures on the two pure metals cobalt and nickel, at the temperature of solid carbon dioxide, -78.4°, and at that of boiling oxygen, -182.5°.

The results, which are given below, show that as the temperature is reduced the value for nickel declines more rapidly than that for cobalt, and hence, that when the mean results are plotted out, the curves steadily approach each other.

The mean specific heats of cobalt and nickel now stand as follows:—

Temperature.	Cobalt.	Nickel.
From 100° to 15°	0.10303	0.10842
" 15° " -78.4°	0.0939	0.0975
" 15° " -182.4°	0.0822	0.0838

and by calculation from the last two results from -78.4 to -182.4, 0.0712, 0.0719.

It seems probable that at absolute zero the values of the products of specific heat, multiplied by atomic weight, would be identical, or differ only by the very small amount due to experimental error.

Note added March 3.—Further experiments made, since the date of communication, upon the metals silver, copper, iron, and aluminium, show, however, that this suggestion will not be realised. The mean specific heat of silver between 15° and 182.4°, for example, is 0.0519, while from 100° to 15° it is 0.0558. The decrease of specific heat at the lower temperature is therefore much less than in the case of cobalt and nickel.

APPENDIX.

The following calculations have been made by E. R. Verity, Assoc. R.C.S., and H. L. Mann, Assoc. R.C.S.:—
If cobalt and nickel were in the states of perfect gases, their specific heats at constant volume would be—

$$k_0 = 0.04123 \text{ for cobalt.}$$

$$k_0 = 0.04145 \text{ for nickel.}$$

This is on the assumption that k_0 multiplied by the atomic weight is the same as for hydrogen. It is not unreasonable to assume that in no state can the substance have a smaller specific heat than k_0 . It is easy to show that for any of the metals the specific heat at atmospheric pressure K is not more than 2 per cent different from the specific heat under any other condition, such as great hydrostatic pressure, to keep its volume constant. Our ignorance of the molecular state of a solid is so great, that we cannot even speculate on how it is that when 1 grm. of cobalt (we have much the same figures for other metals) at 50° C., rises in temperature to 51° C., whether it is allowed to expand freely or is subjected to great hydrostatic pressure which prevents expansion, the energy 0.041 enters it as what may be called the real sensible heat, and the energy 0.062 enters it as some kind of energy of disgregation, necessary because of change of temperature, and having nothing to do with change of volume or pressure. The facts are not explainable by assuming that the atomic weights are wrong, because, as we see from cobalt and nickel, K approaches the value k_0 at low temperatures. Indeed, if the following formula is correctly deduced from the above measurements, we may say that in the solid state the product of the atomic weight and specific heat may be anything between what it is for hydrogen and 2.7 times this amount. The formula is—

$$K = k_0 + \frac{bt^2}{1 + ct^2};$$

where t is the absolute temperature.

	Cobalt.	Nickel.
k_0	0.0412	0.0415
b	1.764×10^{-8}	1.764×10^{-8}
c	2.55×10^{-7}	2.35×10^{-7}

This formula must give fairly correct values of K from -180° C. to 100° C.

Chemical Society.—The Annual General Meeting of the Society, for the election of Officers and other business, will be held on Thursday, March 29th, at 3 o'clock in the afternoon. Presentation of the Longstaff Medal to Professor W. H. Perkin, jun., F.R.S. In the evening the Bunsen Memorial Lecture will be delivered by Sir Henry E. Roscoe, F.R.S. The Chair will be taken at 8.30.

* Bakerian Lecture, read before the Royal Society, March 8, 1900.

HOW TO IGNITE A HYDROGEN JET WITH
NO POSSIBILITY OF EXPLODING THE
GENERATOR.

By C. G. HOPKINS.

THE following are perhaps fair samples of the directions usually found in text-books and manuals for igniting a jet of recently generated hydrogen gas:—

"After the action has continued for a minute or two apply a lighted match" (Remsen, "Introduction to Chemistry," p. 64).

"When all the air is expelled, not less than ten minutes, light the jet of hydrogen" (Newbery, "Laboratory Notebook," eighteenth practice).

"When the gas is coming off freely, light the jet" (Shepard, "Elements of Inorganic Chemistry," p. 38).

As is well known, with any of the above directions, inexperienced students do continue to explode hydrogen generators with annoying frequency, and it is believed that a method of igniting a jet of hydrogen gas with no possible danger of exploding the generator will be welcomed generally by teachers of introductory and qualitative chemistry.

The following method, used by the writer with his classes for a number of years, is absolutely safe, and causes no loss of time whatever:—

As soon as the action begins, collect the escaping gas in a test-tube, and, when it is thought to be full of pure gas, remove 2 or 3 feet from the generator and ignite the hydrogen in the test-tube; then immediately attempt to light the jet of hydrogen with the hydrogen flame contained in the test-tube. If the gas is explosive it will explode in the test-tube and leave no flame. If, on the other hand, a flame remains in the test-tube with which the jet can be ignited, it is certain that the gas in the generator is no longer explosive. Hence, the caution—Never light the hydrogen jet except with the hydrogen flame obtained as just described. The student may try to ignite the jet by this method as often as he wishes until he succeeds, and if the hydrogen is properly generated the jet will be ignited in less than a minute.—*Journal of the American Chemical Society*, xxi., No. 7.

THE PRECIPITATION OF COPPER BY ZINC.*

By JOHN C. SHENGLE and EDGAR F. SMITH.

AT various times during the past year attempts have been made in this Laboratory to make a direct comparison between silver and cadmium, with the hope that in this way the atomic mass of the latter metal might be definitely established. The most carefully purified metallic cadmium in weighed amounts was allowed to act upon various soluble salts of silver. The precipitation of the latter metal was rapid and complete. The results, while very fair in a quantitative respect, could not be used for the purpose designed. The precipitated silver contained cadmium. It was not undissolved portions of the latter, but metal originating from the salt which was acted upon, which salt became in some way encased in the silver so that the most painstaking efforts failed to eliminate it. Nor did it seem to make any difference as to which silver salt was acted upon. Cadmium, in small amounts it is true, but nevertheless cadmium, was invariably discovered in the beautiful deposits of silver.

When copper salts were substituted for silver salts, the cadmium threw out the copper quickly and in calculated amounts, but it also was contaminated with varying quantities of cadmium, so that the scheme originally planned for the determination of the atomic mass of cadmium was abandoned.

This negative experience suggested the idea of testing the copper precipitated by metallic zinc. This being a method recommended for the quantitative estimation of copper, we concluded to ascertain if possible whether it carried or retained any zinc. Pure copper sulphate was prepared, and metallic zinc was also obtained pure by the distillation method of Morse and Burton (*Am. Chem. Journ.*, 1888, x., 148).

The determinations were conducted in the usual manner, but instead of weighing the precipitated copper it was dissolved in nitric acid and estimated by means of the electric current. The liquor poured off from this deposit was examined for the zinc.

Analyses.

I. Twenty c.c. of a copper salt solution, containing 0.1739 grm. of copper, was precipitated by metallic zinc. The deposit of copper was filtered, thoroughly washed, dried, and dissolved in acid, and its solution electrolysed, the filtrate from the copper deposit being used for the determination of any contaminating zinc:—

	Copper present. Grm.	Copper found. Grm.	Zinc found. Grm.
I. . . .	0.1739	0.1742	0.0067

In the second and third determinations the results were—

	Copper present. Grm.	Copper found. Grm.	Zinc found. Grm.
II. . . .	0.1739	0.1741	0.0027
III. . . .	0.2609	0.2612	0.0033

Twenty-two precipitations were made with varying conditions. Zinc was found in all of the precipitated copper. As a rule this method gives fair results, but it is notwithstanding interesting to know that the good results must be due largely to a balancing of errors.

A NEW TEST FOR COCAINE.

By GEORGE L. SCHAEFER.

THERE are two well known tests for determining the freedom of commercial cocaine salts from other coca alkaloids. These are the permanganate test for detecting cinnamyl-cocaine, and the ammonia test, popularly known as McLagan's test, for detecting the presence of the coca alkaloids which are resistant to permanganate. While it is generally admitted that the permanganate test is sufficient to detect the presence of cinnamyl compounds, chemists have expressed some doubt regarding the value of McLagan's test. The writer has for some time been conducting experiments with the object of finding a substitute for McLagan's test which would allow of the rapid and accurate determination of the presence in cocaine salts of the coca alkaloids not indicated by the permanganate test.

As the result of numerous determinations, I have devised a test based on the fact that the chromates of these alkaloids are much less soluble than cocaine chromate, both in water and in water acidulated with hydrochloric acid. The relative solubility of the chromates in acidulated water is about 1 to 500 in the case of cocaine chromate, and 1 in 5000 in the case of the residual alkaloidal chromates.

I therefore offer the following as a simple and satisfactory method of determining the purity of cocaine salts:—0.05 grm. cocaine hydrochloride is dissolved in 20 c.c. of distilled water, mixed with 5 c.c. of a 3 per cent solution of chromic acid, and to the mixture 5 c.c. of a 10 per cent solution of hydrochloric acid are added. It is advisable to keep the temperature of the solution at 15° C. If the cocaine hydrochloride be pure a clear solution will result. If other than traces of foreign coca bases be present the solution becomes cloudy at once, or in a few minutes, according to the amount of impurity present.

It is advisable to make the test side by side with a specimen of known purity for comparison.—*Journal of the American Chemical Society*, xxi., No. 7.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, vol. xxi., No. 10.

ON THE NORMAL PRESENCE AND THE LOCALISATION OF ARSENIC IN THE ORGANS OF ANIMALS.

By A. GAUTIER.

VARIOUS circumstances have led me to study the action of arsenical preparations on the animal economy; I have particularly observed that cacodylic acid, $\text{As}(\text{CH}_3)_2\text{O}_2\text{H}$, obtained by Bausen in 1843—an acid which has remained unemployed since its discovery—is of remarkable efficacy in certain specific diseases (anæmia, malaria, goitre, phthisis), although all the poisonous and even chemical properties of the arsenic have disappeared in this very soluble body, which, however, contains 54.3 per cent of metalloidal arsenic.

Since my communication to the Academy of Medicine last June, cacodylic acid is being made in France in a state of great purity, and is now sold by hundreds of kilogrammes.

In the course of this research I was led to ask by what mechanism does arsenic act on the economy. Various considerations led me to think that it fixes on the nucleic matter where it doubtless replaces phosphorus to a certain extent. On the other hand, remembering the fact that in certain diseases of the thyroid gland a general treatment with arsenic and iodine is advantageous; also that arsenic and iodine are often associated in nature, and not forgetting the fact that, in the normal state, iodine exists in a fairly large quantity in the thyroid gland, it appeared to me that it might be possible for arsenic to be one of the constituent principles of this gland, having the same value as the iodine, and perhaps normally present in other tissues of the body.

These ideas have been confirmed by my researches.

I have discovered that arsenic exists normally and in smaller proportions in the thymus and the brain, and as traces in the skin and hair.

The normal existence of arsenic in animal bodies appear to contradict all the teachings of toxicology. Thousands of careful experiments have been made on human beings without detecting arsenic in the organs. These facts are explained, on the one hand, by the imperfect methods generally employed for the destruction of the organic matter (Cl ; $\text{ClO}_2\text{K} + \text{HCl}$; attack by *aqua regia*, and distillation, &c.), methods which, on account of the disengagement of volatile chlorinised fumes, cause the partial or complete loss of the small quantities of arsenic.

It is, on the other hand, explained by the consideration that arsenic, according to the experiments I am about to describe, is absent from most of the human organs. It is only met with in the thyroid, the thymus, the brain, and as traces in the bones and skin.

I do not speak for the organs I have not yet examined.

I have vainly tested for arsenic in 100 to 200 grms. of the following organs:—

- The liver of sheep, dogs, pigs, and calves;
- The spleen of dogs and oxen;
- Loins of pigs;
- The pituitary gland of sheep;
- The flesh of dogs;
- The stomachic mucus;
- And pig's blood (250 grms. defibrinated).

I have never found arsenic in these organs, or, if present, it was in a state of such dilution that my method, which enables one hundredth of a milligramme to be detected in 100 grms. of tissue, showed no trace.

Arsenic is, on the other hand, constantly present in the thyroid gland, and although its quantity is small I have since the commencement of this research been able to detect it in only 5.2 grms. of the fresh thyroid gland of the dog.

45 grms. of the fresh thyroid of a pig gave an arsenic ring weighing about 0.3 m.grms.; or 0.67 m.grms. per 100 grms. of the fresh organ, or nearly seven-tenths of a m.grm.

per kilo. This would be about 3 m.grm. per kilo. of the dried gland.

100 grms. of the thyroid of sheep gave me an arsenic ring weighing 0.05 grm.; which corresponds to 2 m.grms. of arsenic per kilogram. of the dried gland.

All these figures are a little low, which has since been explained by a small error in my method.

After having made the correction, I operated on 127 grms. of human thyroid gland taken from six persons who had not taken any metallic medicaments, and, above all, no arsenic during their illness. I obtained a ring of arsenic weighing nearly 1 m.grm. (0.95 m.grm.).

All these experiments were verified by repeating them twice with sheep's liver totally free from arsenic, as a check. It was treated exactly like the thyroid. All these check experiments gave negative results.

Arsenic thus exists normally in the thyroid gland of herbivorous and carnivorous animals. In the case of man, we have found about 1 m.grm. per 127 grms.; that is, 1/127,000th part of the weight of the fresh thyroid. This small quantity suffices for the gland to perform its functions which are of importance, and depend on the constant presence of arsenic in this specific organ, as there is no thyroid without arsenic and no health without the thyroid.

The gland no doubt obtains this important element from the food we take, though in a state of extreme dilution. Stein (*Journ. f. Prakt. Chem.*, li., p. 302; liii., p. 37) has, in fact, recognised its presence in a number of vegetables—rye-straw, potatoes, turnips, cabbages, &c. I have recently found it myself in several foods of animal origin, especially milk.

Arsenic exists in considerable quantity in the thyroid gland, in smaller quantity in the thymus and the brain, and as traces in the skin. In what form does it exist in these organs?

I thought that, seeing the chemical analogies, arsenic ought to be found in the thyroid, especially in the form of arsenical nucleines forming the nucleus of the cells (*kernucleines*), or the basophil granulations of the protoplasm (*paranucleines*). It might also form part of certain lecithines.

To make sure of the existence of arsenic in the nuclein of the thyroid, I separated these nucleines by pepsic digestion.

This, as is known, peptonises the albumenoids of the protoplasm while the nucleines remain in the residue. In this manner I digested 100 grms. of fresh thyroid from sheep with 0.5 grm. of a pepsic liquor. After fifty-four hours at 38°, there remained a magma formed of indigestible materials, among which could be distinguished an iron grey pulverulent matter, which was found to be very much iodised. The peptones formed and the residue were separated by filtration. I satisfied myself that the peptones did not contain a trace of arsenic. The residue was put to digest at 38° with ammonia diluted with 40 times its volume of water, to dissolve the nucleines; it was then filtered, and the solution precipitated with acetic acid.

The nucleines thus separated, which I found to be very rich in iron (2 m.grms. sufficed for estimating this element), were collected on a filter, washed, and dried. 1.21 grms. of these nucleines, weighed in the dried state, the quantity extracted from 100 grms. of moist thyroid, gave a very good ring of arsenic.

There therefore exist in the normal state in the thyroid, and in much smaller proportion in the thymus, the brain, and the skin, arsenical nucleines (*arsenucleines*), which are liable to be split up by acids into *arsenucleic acids* and albumenoids. These *arsenucleic acids* (and the *arsenucleines* themselves) behave as ferments, if we apply the observations of Lillienfeld on the ordinary phosphorised leuco-nucleines. Their constant presence in the normal thyroid gland shows us the necessity of arsenical treatment when illness, or the destruction of the gland, in part or totally deprives the economy of the arsenic which is necessary to it.

Then appears more particularly myxœdemia, which specially affects the thyroid, the brain, and the skin; that is to say, the three organs in which I have observed that arsenic always exists in the normal state.

The proof of the normal existence of arsenic in the animal economy is important not only in furnishing the proof, drawn from the constant presence of arsenic in the thyroid, the brain, and the skin, of the definite relations, chemical and functional, which unite these three organs; but it also shows the influence that almost infinitesimal doses of certain active elements have on the functions of animal life. One human thyroid gland contained about 0.17 m.grm. of arsenic; for a man weighing 67 kilograms, these 17 hundredths of a m.grm., represent 1/400,000,000th of the total mass. This four hundred millionth is enough to enable the gland to operate normally and the health is maintained. The health suffers when the arsenic diminishes.

There is still another point arising from this research, and that is to decide what specific functions, more or less latent, are proceeding in our organs, thanks to the presence of certain specific elements of which the major part are still probably ignored.

Among these elements of which we are already aware, I would mention manganese, a principle of oxidising fermentation according to M. Bertrand; iodine, a specific element functioning in the thyroid; arsenic, which I have just found in the arsenical nucleines; fluorine, which is found in the bone cells. There is therefore still room for research in every organ, and, thanks to the most delicate methods, for the different elements that we might consider likely, by being substituted as above for the chemical analogues, to modify the functioning of the organ by reason of certain special needs, such would be selenium in place of sulphur; negative sulphur substituted for oxygen; copper, zinc, or manganese replacing iron; phosphorus, arsenic, or even vanadium itself playing the part of nitrogen in the more or less complex molecules. This forms a complete new branch of biological chemistry full of promise for the future.

I need hardly mention what would follow these possibilities from the etiological and therapeutical point of view of illnesses.

Finally, toxicologists will have, from the medico legal-expert point of view, to take notice of these observations which have established the normal existence of arsenic in certain organs, as well as its complete absence from the major part of the tissues and the blood of animals.

It is necessary to add, for the benefit of those who wish to repeat the experiments, that the detection of arsenic in the organs should be made, not by the methods too often used, by which the chlorinised fumes carry off and possibly lose the arsenic, but by the much more certain method described by me in 1876 (*Ann. Chim. Phys.*, Series 5, viii., p. 384)—a method which I have further improved during my present research.—*Bull. Soc. Chim.*, Series 3, xxxiii., No. 1.]

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1900.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the

maines of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month has been exceptionally heavy, no less than 4.23 inches having been measured; the average fall for February is 1.76 inches, we therefore have an excess of 2.47 inches; the total excess for the first two months of this year is now 2.61 inches, or 66.5 per cent on the thirty years' average.

Our bacteriological examinations of 492 samples have given the results recorded in the following table; we have also examined 32 other samples, from special standpipes, &c., making 524 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	682
New River, filtered (mean of 116 samples) ..	18
Thames, unfiltered (mean of 24 samples) ..	8086
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 270 samples) ..	66
Ditto ditto highest	992
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	692
River Lea, from the East London Company's clear-water wells (mean of 34 samples) ..	13

The exceptionally high rainfall of 4.23 inches during the month, following a long drought at this time of the year, has resulted in the organic carbon being higher, and the bacteriological purity of some of the filtered waters being lower, than the average of the last few months. This has been especially the case in three of the Thames-derived waters, the filter wells of which on some occasions have given abnormally high numbers. So far as we can ascertain, the working of the filters has been conducted with all the customary care and precautions. Similar abnormal results have usually followed the breaking up of a long drought. On careful examination it is satisfactory to know that the organisms in these exceptional samples are harmless river microbes, and we have been unable to detect among them any other kind of organism. As on previous occasions, the filter beds that gave these abnormal samples of water were again in a few days working satisfactorily.

It will be observed that, in spite of the floods, the bacterial quality of the New River and the Lea supply has been exceptionally good, and amongst the 150 samples of these waters examined no abnormal results were found.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

The Contaminated Waters of the Wells of Guillotière and Brotteaux à Lyon.—H. Causse.—The waters of the wells of Guillotière and Brotteaux have undoubtedly been the cause of typhoid fever. The author, therefore, has examined the waters, and perceived the bacillus *Bacterium termo* to be present in large quantities. He found no albumenoids in the waters, nor nucleo-proteids. —*Comptes Rendus*, cxxx., No. 9.

LIQUID HYDROGEN.*

By Professor DEWAR, M.A., LL.D., F.R.S., &c.

FROM the year 1878, when the experiments of Cailletet and Pictet were attracting the attention of the scientific world, it became a common habit in text-books to speak of all the permanent gases, without any qualification, as having been liquefied, whereas these experimentalists, by the production of an instantaneous mist in a glass tube of small bore, or a transitory liquid jet in a gas expanding under high compression into air, had only adduced evidence that sooner or later the static liquid form of all the known gases would be attained. Neither Pictet nor Cailletet in their experiments ever succeeded in collecting any of the permanent gases in that liquid form for scientific examination. Yet we meet continually in scientific literature with expressions which lead one to believe that they did. For instance, the following extract from the *Proceedings of the Royal Society*, 1878, illustrates this point very well:—"This award (Davy Medal) is made to these distinguished men (Cailletet and Pictet) for having independently and contemporaneously liquefied the whole of the gases hitherto called permanent." Many other quotations of the same kind may be made. As a matter of fact six years elapsed, during which active investigation in this department was being prosecuted, before Wroblewski and Olszewski succeeded in obtaining oxygen as a static liquid, and to collect liquid hydrogen, which is a much more difficult problem, has taken just twenty years from the date of the Pictet and Cailletet experiments.

Wroblewski made the first conclusive experiment on the liquefaction of hydrogen in January, 1884. He found that the gas cooled in a capillary glass tube to the boiling point of oxygen, and expanded quickly from 100 to 1 atmosphere, showed the same appearance of sudden ebullition lasting for a fraction of a second, as Cailletet had seen in his early oxygen experiments. No sooner had the announcement been made, than Olszewski confirmed the result by expanding hydrogen from 190 atmospheres, previously cooled to the temperature given by liquid oxygen and nitrogen evaporating under diminished pressure. Olszewski, however, declared in 1884 that he saw colourless drops, and by partial expansion to 40 atmospheres, the liquid hydrogen was seen by him running down the tube. Wroblewski could not confirm Olszewski's results, his hydrogen being always obtained in the form of what he called a "liquide dynamique," or the appearance of an instantaneous froth. Olszewski himself seven years later repeated his experiments of 1884 on a larger scale, confirming Wroblewski's results, thereby proving that the so-called liquid hydrogen of the earlier experiments must have been due to some impurity. The following extract from Wroblewski's paper states very clearly the results of his work on Hydrogen:—

"L'hydrogène soumis à la pression de 180 atm. jusqu'à 190 atm., refroidi par l'azote bouillant dans la vide (à la température de sa solidification) et détendu brusquement sous la pression atmosphérique présente une mousse bien visible. De la couleur grise de cette mousse, où l'œil ne peut distinguer des gouttelettes incolores, on ne peut pas encore deviner quelle apparence aurait l'hydrogène à l'état de liquide statique et l'on est encore moins autorisé à préciser s'il a ou non une apparence métallique. J'ai pu placer dans cette mousse ma pile thermo-électrique, et j'ai obtenu suivant les pressions employées des températures de -208° jusqu'à -211° C. Je ne peux pas encore dire dans quelle relation se trouvent ces nombres avec la température réelle de la mousse ou avec la température d'ébullition de l'hydrogène sous la pression atmosphérique puisque je n'ai pas encore la certitude que la faible durée de ce phénomène air permis à la pile de se refroidir complètement. Néanmoins, je crois aujourd'hui de mon devoir

de publier ces résultats, afin de préciser l'état actuel de la question de la liquéfaction de l'hydrogène."—*Comptes Rendus*, 1885, c., 981.

It is well to note that the lowest thermo-electric temperature recorded by Wroblewski during the adiabatic expansion of the hydrogen (namely, -211°) is really equivalent to a much lower temperature on the gas-thermometer scale. The most probable value is -230° , and this must be regarded as the highest temperature of the liquid state, or the critical point of hydrogen, according to his observations. In a posthumous paper of Wroblewski's on "The Compression of Hydrogen," published in 1889, an account appears of further attempts which he had made to liquefy hydrogen. The gas compressed to 110 atmospheres, was cooled by means of liquid nitrogen under exhaustion to -213.8° . By suddenly reducing the pressure, as low a temperature as -223° on his scale was recorded, but without any signs of liquefaction. This expansion gives a theoretical temperature of about 15° absolute in the gas particles. The above methods having failed to produce static hydrogen, Wroblewski suggested that the result might be attained by the use of hydrogen gas as a cooling agent. From this time until his death in the year 1888, Wroblewski devoted his time to a laborious research on the isothermals of hydrogen at low temperatures. The data thus arrived at enabled him, by the use of Van der Waal's formulae, to calculate the critical constants, and also the boiling point of liquid hydrogen.

Olszewski returned to the subject in 1891, repeating and correcting his old experiments of 1884, which Wroblewski had failed to confirm, using now a glass tube 7 m.m. in diameter instead of one of 2 m.m. as in the early trials. He says: "On repeating my former experiments, I had no hope of obtaining a lower temperature by means of any cooling agent, but I hoped that the expansion of hydrogen would be more efficacious, on account of the larger scale on which the experiments were made." The results of these experiments Olszewski describes as follows: "The phenomenon of hydrogen ebullition, which was then observed, was much more marked and much longer than during my former investigations in the same direction. But even then I could not perceive any meniscus of liquid hydrogen." Further, "The reason for which it has not hitherto been possible to liquefy hydrogen in a static state, is that there exists no gas having a density between those of hydrogen and of nitrogen, and which might be for instance 7—10 ($H=1$). Such a gas could be liquefied by means of liquid oxygen or air, as cooling agent, and be afterwards used as a frigorific menstruum in the liquefaction of hydrogen."

Professor Olszewski, in 1895, determined the temperature reached in the momentary adiabatic expansion of hydrogen at low temperatures, just as Wroblewski had done in 1885, only he employed a platinum-resistance thermometer instead of a thermo-junction. For this purpose he used a small steel bottle of 20 or 30 c.c. capacity, containing a platinum-resistance thermometer; in this way, the temperatures registered were regarded as those of the critical and boiling points of liquid hydrogen, a substance which could not be seen under the circumstances and was only assumed to exist for a second or two during the expansion of the gaseous hydrogen in the small steel bottle.

The results arrived at by Wroblewski and Olszewski are given in the following table, and it will be shown later on that Wroblewski's constants are nearest the truth.

	Wroblewski, 1885.	Olszewski, 1895.
Critical temperature..	-240°	-234°
Boiling point	-250°	-243°
Critical pressure.. ..	13 atm.	20 atm.

The accuracy of Wroblewski's deductions regarding the chief constants of liquid hydrogen following from a study of the isothermals of the gas is a signal triumph for the

* A Lecture delivered at the Royal Institution, January 20, 1899.

theory of Van der Waals, and a monument to the genius of the Cracow physicist. From these results we may safely infer that, supposing a gas is hereafter discovered in small quantity four times more volatile than liquid hydrogen, having a boiling point of about 5° absolute, and therefore incapable of direct liquefaction by the use of liquid hydrogen, yet by a study of its isothermals we shall succeed in finding out its most important liquid constants, although the isolation of the real liquid may for the time be impossible.

In a paper published in the *Philosophical Magazine*, September, 1884, "On the Liquefaction of Oxygen and the Critical Volumes of Fluids," the suggestion was made that the critical pressure of hydrogen was wrong, and that instead of being 99 atmospheres (as deduced by Sarrau from Amagat's isothermals) the gas had probably an abnormally low value for this constant. This view was substantially confirmed by Wroblewski finding the critical pressure of 13.3 atmospheres, or about one-fourth of that of oxygen. The *CHEMICAL NEWS*, September 7, 1894,

evidently giving off hydrogen, because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent of air is similarly treated, the result is a white solid matter (solid air) along with a clear liquid of low density, which is so exceedingly volatile that no known device for collecting it has been successful." This was in all probability the first liquid hydrogen obtained, and the method is applicable to other difficultly liquefiable gases.

Continuing the investigations during the winter of 1894, and the greater part of 1895, the author read a paper before the Chemical Society in December of that year, entitled: "The Liquefaction of Air and Research at Low Temperatures" (*Proc. Chem. Soc.*, 1895, No. 158), in which occasion was taken to describe for the first time the mode of production and use of a Liquid Hydrogen Jet. At the same meeting Professor William Ramsay made an announcement of a sensational character, which amounted to stating that my hydrogen results had been not only anticipated but bettered. The statement made to the

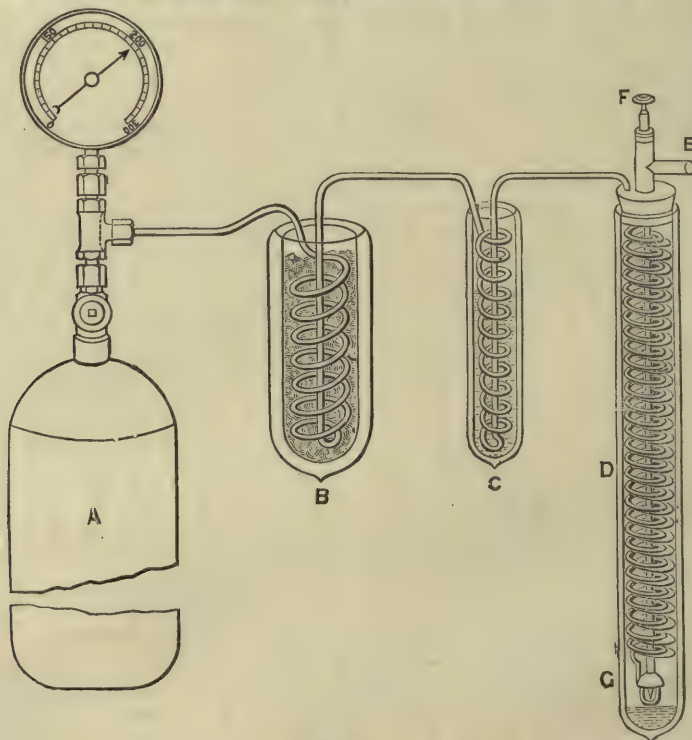


FIG. 1.

contains an account of the stage the author's hydrogen experiments had reached at that date. The object was to collect liquid hydrogen at its boiling point, in an open vacuum vessel, which is a much more difficult problem than seeing it in a glass tube under pressure and at a higher temperature. In order to raise the critical point of hydrogen to about -210° , from 2 to 5 per cent of nitrogen or air was mixed with it. This is simply making an artificial gas containing a large proportion of hydrogen which is capable of liquefaction by the use of liquid air. The results are summed up in the following extract from the paper:—"One thing can, however, be proved by the use of the gaseous mixture of hydrogen and nitrogen, namely that by subjecting it to a high compression at a temperature of -200° and expanding the resulting liquid into air, a much lower temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under the conditions, a paste or jelly of solid nitrogen,

Society by Professor Ramsay, reads as follows:—"Professor Olszewski had succeeded in liquefying hydrogen, and from unpublished information received from Cracow, he (Ramsay) was able to state that a fair amount of liquid had been obtained, not as a froth, but in a state of quiet ebullition, by surrounding a tube containing compressed hydrogen by another tube also containing compressed hydrogen at the temperature of oxygen boiling at a very low pressure. On allowing the hydrogen in the middle jacket suddenly to expand, the hydrogen in the innermost tube liquefied, and was seen to have a meniscus. Its critical point and its boiling point, under atmospheric pressure, were determined by means of a resistance thermometer."—*Proc. Chem. Soc.*, 1897—1898, No. 195.

This announcement of Professor Ramsay's had from its very specific and detailed experimental character the merit of the appearance of being genuine, although it was never substantiated, either by the production of the Cracow document, or by any subsequent publication of such important

results by Professor Olszewski himself. My observation at the time on Professor Ramsay's communication was that quotations had been made in my paper from the most recent publications of Professor Olszewski in which he made no mention of getting "Static Hydrogen or of seeing a meniscus" or of getting as Professor Ramsay alleged "a fair amount of liquid, not as a froth, but in a state of quiet ebullition." To achieve such a result would require a very different scale of experiment from anything Professor Olszewski had so far described. Naturally an early corroboration of the startling statement made by Professor Ramsay as to this alleged anticipation was expected, but strange to say Professor Olszewski published no confirmation of the experiments detailed by Professor Ramsay in scientific journals of date immediately preceding my paper or during the following years, 1896, 1897, or up to May, 1898. The moment the announcement was made by me to the Royal Society in May, 1898, that, after years of labour, hydrogen had at last been obtained as a static liquid, Professor Ramsay repeated the story to the Royal Society that Olszewski had anticipated my results (basing the assertion solely on the contents of the old letter received some two and a half years before), in spite of the fact that during the interval he, Professor Ramsay, must have known that Professor Olszewski had never corroborated in any publication either the form of the experiments he had so minutely described, or the results which were said to follow. Challenged by me at the Royal Society Meeting on May 12, 1898, to produce Olszewski's letter of 1895, he did not do so, but at the next meeting of the Society, Professor Ramsay read a letter he had received during the interval from Professor Olszewski, denying that he had ever stated that he had succeeded in producing static liquid hydrogen. This oral communication of the contents of the new Olszewski letter (of which it is to be regretted there is no record in the published proceedings of the Royal Society) is the only kind of retraction Professor Ramsay has thought fit to make of his published mis-statements of fact. No satisfactory explanation has yet been given by Professor Ramsay of his twice-repeated categorical statements made before scientific bodies of the results of experiments which, in fact, had never been made by their alleged author. The publicity that has been given to this controversy makes it imperative that the matter should not be passed over, but once for all recorded.

The report of a Friday Evening Discourse on "New Researches on Liquid Air" (*Proc. Roy. Inst.*, 1896), contains a drawing of the apparatus employed for the production of a jet of hydrogen containing visible liquid. This is reproduced in Fig. 1. A represents one of the hydrogen clinders; B and C, vacuum vessels containing carbonic acid under exhaustion, and liquid air respectively; D is the coil, G the pin-hole nozzle, and F the valve. By means of this hydrogen jet, liquid air can be quickly transformed into a hard solid. It was shown that such a jet could be used to cool bodies below the temperature that it is possible to reach by the use of liquid air, but all attempts to collect the liquid hydrogen from the jet in vacuum vessels failed. No other investigator improved on my results (*Proc. Chem. Soc.*, 1895, No. 158), or has indeed touched the subject during the last three years. The type of apparatus used in these experiments worked well, so it was resolved to construct a much larger liquid-air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen. This apparatus took a year to build, and many months have been occupied in the testing and preliminary trials. The many failures and defeats need not be detailed.

(To be continued).

Determination of Sulphur in Sulphites.—A. Bourgougnon (*J. Am. Chem. Soc.*, xx, 469).—The sulphite in dilute hydrochloric acid solution is treated with a solution of hydrogen peroxide, and the sulphuric acid formed is precipitated and weighed as barium sulphate.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

THIRD PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE AND OXIDE.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

(Concluded from p. 127).

Critical Review of Earlier Work.

In the light of the information gained during the protracted investigation which has just been described, it is possible to discover the reasons for many of the unusual discrepancies in the older work upon the atomic weight of cobalt. Following is a chronological list of this work, with references to the original articles. The atomic weight of oxygen, upon which the appended values are based, is taken as 16.000.

1826	Rothhoff (<i>Pogg. Ann.</i> , viii., 184)	59
1857	Schneider (<i>Pogg. Ann.</i> , ci., 387)	60.0
1858	Marignac (<i>Bibl. Univ. de Geneve</i> , i., 372) ..	58.8
1860	Dumas (<i>Ann. Chem. Pharm.</i> , cxiii., 25) ..	59.1
1863	Russell (<i>Journ. Chem. Soc.</i> , [2], i., 51) ..	58.7
1866	Sommaruga (<i>Sitz. Wien. Akad.</i> , liv., [2], 50)	60.
1867	Winkler (<i>Zeit. Anal. Chem.</i> , vi., 18)	59.4
1867	Russell (<i>Journ. Chem. Soc.</i> , [2], vii., 294) ..	59.1?
1868	Weselsky (<i>Ber. d. d. Chem. Gesell.</i> , ii., 592)	59.1
1871	Lee (<i>Am. Journ. Sci. and Arts</i> , [3], ii., 44)	59.2
1886	Zimmermann (<i>Ann. der Chem.</i> , ccxxxii., 324)	58.9
1889	Krüss and Schmidt (<i>Ber. d. d. Chem. Gesell.</i> , xxii., 11)	—
1889	Winkler (<i>Ber. d. d. Chem. Gesell.</i> , xxii., 891)	—
1891	Remmler (<i>Zeit. Anorg. Chem.</i> , ii., 221) ..	58.8
1892	Schützenberger (<i>Comptes Rendus</i> , cxiv., 1149)	60.1
1893	Winkler (<i>Zeit. Anorg. Chem.</i> , iv., 10)	59.8
1894	Winkler (<i>Zeit. Anorg. Chem.</i> , iv., 462) ..	59.5
1895	Winkler (<i>Zeit. Anorg. Chem.</i> , viii., 1)	—
1895	Winkler (<i>Zeit. Anorg. Chem.</i> , viii., 291) ..	—
1896	Hempel and Thiele (<i>Zeit. Anorg. Chem.</i> , xi., 73)	58.9
1897	Richards and Baxter (<i>Zeit. Anorg. Chem.</i> , xvi., 362)	59.0
1898	Winkler (<i>Zeit. Anorg. Chem.</i> , xvii., 236) ..	—
1899	Richards and Baxter (<i>Proc. Amer. Acad.</i> , xxxiv., 351)	59.0
1899	Richards and Baxter (the present paper) ..	59.0

All except four of these investigations were accompanied by similar ones upon the atomic weight of nickel, and in general the criticisms made by Richards and Cushman in a recent paper upon this subject may be applied unchanged to the present argument. It is only necessary to call attention here to the features in which differences existed.

The favourite method for the determination of both constants has been the reduction of the oxides. It is evident from our work upon this method that Russell's cobaltous oxide (1863) must have been contaminated with a higher oxide; that Zimmermann's material (1886), treated with greater care in more perfect apparatus, was more nearly normal, although still impure; and that Schützenberger (1892) must have driven off some of the oxygen, which should have been weighed, by his employment of a high temperature. It was reserved for Hempel and Thiele (1895) to discover by varying the conditions of work that cobaltous oxide was incapable of giving constant results, although they did not attempt to find the reason of the inconstancy. Their irregular observations were really a proof of the thoroughness and care of their work, while the wonderful constancy of Zimmermann's results simply shows a constancy of imperfect conditions.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. XXXV., No. 3, 1899.

The far greater dissociation tension of the higher oxide of nickel makes the method much less dangerous in this case; hence the similar results for the atomic weight of nickel are both more concordant and more nearly correct than those for the atomic weight of cobalt.

The four investigations which had no parallel in the case of nickel were those of Sommaruga, Weselsky, Remmler, and Hempel and Thiele. The first of these need not claim serious attention, for there can be no doubt that the result (60.0) is far too high. Weselsky's contribution was very similar to Lee's, which has been treated in Richards and Cushman's criticism. Since the work was obviously crude and incomplete, we must ascribe its accurate average result (58.96) to a compensation of errors.

Two more investigations remain to be considered. In 1891, when the "Gnomium" dispute was at its height, Remmler entered the fray. He fractionated cobaltous hydrate by treating a large quantity of this precipitate with strong ammonia. Each fraction was subjected to a protracted purification, which, although effective in removing heavy metals, introduced more impurity than it removed. His final solution of cobaltous nitrate, from which he formed the oxide by ignition, contained the alkali and silica taken up by at least six successive evaporations to dryness in glass or porcelain, in three of which the solution was ammoniacal. With such hopelessly contaminated material, it is no wonder that the results from twenty-four fractions varied between limits which were nearly 1 per cent apart. As his methods of igniting the monoxide to constant weight in an inert gas was subject to the same errors which have been discussed in the case of Russell and Zimmermann, no further comment is necessary. The average of 24 determinations was 58.80.

Hempel and Thiele, in 1895, at first attempted to find the ratio CoO : Co from analyses of the monoxide. This part of their research has been already discussed.

The remainder of their work consisted in the quantitative preparation and analysis of cobaltous chloride. They were unable to prepare it in a wholly anhydrous condition, and realised this fact; hence the part of their calculation depending upon the weight of the chloride was unsatisfactory. The final step of their investigation was the weighing of the argentic chloride obtainable from the chloride combined with a known weight of cobalt. Although not wholly satisfactory, this part of their research far excelled the earlier work of a similar kind (Dumas) and yielded one of the most trustworthy values for the atomic weight of cobalt (59.91 to 59.94) which had been obtained at that time.

It is clear, from a careful consideration of the details just referred to, that all the wide variations in the older results are explicable. Hence no serious argument exists against the atomic weight of cobalt (58.995, if O = 16) determined by our analyses of cobaltous bromide. Since, moreover, the still more recent results which the chloride (less than 59.05) and oxide (58.93 to 59.07) confirm this value, one may assume that it is not greatly in error. In any case, the Harvard analyses of the bromides of nickel and cobalt must stand and fall together, for they were made by methods essentially similar; and they must at least give the ratio of the atomic weights (58.706 : 58.995) with some approach to accuracy. Each of these numbers has found quite independent support for its actual as well as the relative value, so that for the present the study of these atomic weights will not be pursued further in this Laboratory.

Glycerides of the Monobasic Acids in C_{2n}.—L. T. C. Scheij.—This paper is a summing up of the densities, molecular volumes, and indices of refraction of water, and glycerin, and butyric, caproic, caprylic, capric, lauric, myristic, palmitic, and stearic acids, as well as of the triglycerides derived from these acids.—*Revue Trav. Ch. P.-B.*, xviii., p. 169.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 1st, 1900.

Professor THORPE, F.R.S., President, in the Chair.

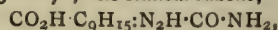
(Concluded from p. 130).

*34. "Some Acids obtained from α -Dibromocamphor." By ARTHUR LAPWORTH and EDGAR M. CHAPMAN.

Camphonic acid is the name the authors propose for the acid obtained by hydrolysing α -monobromocampholid (compare Forster, *Trans.*, 1896, lxi., 51). It has the formula C₁₀H₁₆O₃, crystallises from ethyl acetate in prisms melting at 194°, and appears to be dimorphous. It has all the properties of a ketonic acid, a fact which shows conclusively that α -monobromocampholid contains the group—

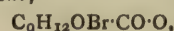


The oxime, C₁₀H₁₅N·OH, forms slender needles melting at 125—127°; the semicarbazone,—

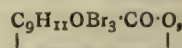


crystallises in flattened needles which melt and decompose at 222—223°. The phenylhydrazones and p-bromophenylhydrazones were obtained as colourless pulverulent substances, which yielded well characterised sodium salts.

Dibromocamphonic acid, C₉H₁₃OBr₂·CO₂H, is obtained on adding bromine to a solution of camphonic acid in chloroform; it melts and decomposes at 144°. Monobromocamphonolactone,—

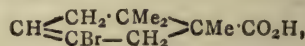


is formed when the sodium salt of the dibromo-acid is boiled with water; it crystallises in glistening needles or prisms melting at 110—111°. Tribromocamphonolactone,—

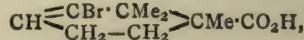


produced by gently warming dibromocamphonic acid with excess of bromine, melts at 166—167°.

The formation of a tribromolactone from camphonic acid, taken in conjunction with the rest of the evidence relating to the derivatives of camphorenic acid, shows, with some degree of probability, that bromocamphorenic acid has the formula—

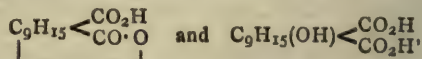


and not—



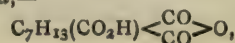
for which a preference has been expressed by one of the authors (*Trans.*, 1899, lxxv., 1139).

Camphonic acid unites with hydrocyanic acid, and on treating the product with hydrochloric acid, two new acids,—



are obtained. The former crystallises in long needles melting at 144—145°; the latter forms orthorhombic plates melting, with formation of an anhydride, at 207°, and cannot be obtained by hydrolysing the lactonic acid.

Homocamphorenic acid is rapidly attacked by bromine at 140°, but the product is nearly free from bromine, and is probably a mixture of lactonic acids. Trimethyl homocamphoronate, C₇H₁₃(CO₂Me)₃, was obtained on treating the acid with phosphorus pentabromide and bromine, and subsequently pouring into methyl alcohol; it boils at 305—308° under atmospheric pressure. β -Anhydrohomocamphorenic acid,—



It is generally agreed that the molecule of camphoric acid contains two dissimilar asymmetric carbon atoms, which are links in a closed chain, and have attached to them the ortho- and allo-carboxyl groups respectively. On electrolysis of potassium allo-ethyl *d*-camphorate, an etheral product is obtained, the lowest boiling portions of which have only the allo-carboxyl group and the allo-asymmetric carbon atom, the ortho-asymmetric carbon atom having lost its asymmetry by the removal of the ortho-carboxyl group. This lowest boiling fraction has a strong positive rotation, namely $[\alpha]_{\text{D}} = +29.8^\circ$, which must be due to the allo-symmetric carbon atom. If now the allo-asymmetric carbon atom of *l*-isocamphoric acid has the opposite configuration to that of *d*-camphoric acid, the rotation⁷ of the corresponding fraction from the

etheral product of electrolysis of potassium allo-ethyl *l*-isocamphorate should be of the same dimensions but of opposite sign,—that is, it should be strongly negative. The rotation of the substance actually produced is, however, strongly positive, namely, $[\alpha]_D = +20.9^\circ$, although the original substance and the impurities in the low boiling fraction have a large negative rotation. It appears, therefore, that the allo-asymmetric carbon atoms in *d*-camphoric acid and *l*-isocamphoric acid have the same configuration, and that the ortho-asymmetric carbon atoms have opposite configurations.

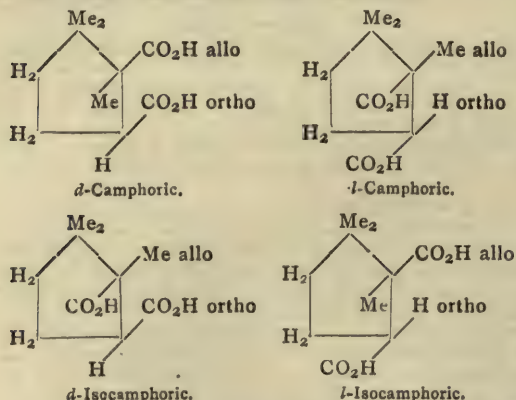
Assuming the configuration RR' for ordinary camphoric acid, we can represent the configuration of all the camphoric acids by the following scheme:—

	<i>d</i> -Camphoric.	<i>l</i> -Camphoric.	<i>d</i> -Iso-camphoric.	<i>l</i> -Iso-camphoric.
Ortho..	R	L	R	L
Allo..	R'	L'	L'	R'

39. "The Constitution of Camphoric Acid." By JAMES WALKER.

The Perkin-Bouveault formula for camphoric acid is considered by the author as the most satisfactory hitherto proposed. It represents camphoric acid as a derivative of succinic acid, and thereby accounts in a simple manner for the nature of the unsaturated compounds obtained by electrolysis of the sodium alkyl salts of camphoric acid. In particular, the formulæ derived from it for campholytic and isolaunonic acids represent these substances as $\alpha\beta$ -unsaturated acids without an asymmetric carbon atom, in accordance with their chemical behaviour and optical inactivity. Perkin's second formula and Bredt's formula, which represent camphoric acid as a derivative of glutaric acid, not only fail to explain the electrolytic production of campholytic and isolaunonic acids, but represent these acids as having an asymmetric carbon atom, and therefore essentially ad hoc. Analogy and experiment alike exclude the assumption of a possible racemism.

The configuration of the camphoric acids on the basis of the Perkin-Bouveault formula is as follows:—



The dissociation constant of camphoric acid, which seems to be very small for a derivative of succinic acid or glutaric acid, is shown to be only apparently abnormal. The rise in the constant of succinic and glutaric acids when hydrogen is replaced by alkyl, is due to the approximation of the carboxyl groups, and is not the primary effect of the substitution. If the molecule acquires rigidity by ring formation or multiple linking, this approximation is prevented, and the primary effect of the substitution is observed, which is in general a diminution of the constant, as in monocarboxylic acids. It is therefore to be expected that the dissociation constant of camphoric acid, which has one tertiary and one secondary carboxyl, should be less than that of succinic or glutaric acids, which have two primary carboxyls. The very small values of the monocarboxylic acids derived from camphoric acid confirm this view.

40. "On the Presence of Invertase in Plants of the Graminae." (I). By JAMES O'SULLIVAN.

The difficulty of extracting invertase from the living cells of plants which were proved to contain it was the first point considered. This was overcome in the following manner:—Portions of the roots, culms, and leaves of wheat, oats, and maize plants at various stages of growth, after being well washed with chloroform water, were digested in the cold, and at $49-50^\circ$, for different lengths of time, with a cane-sugar solution saturated with chloroform, and the amounts of cane-sugar hydrolysed were determined by the cupric oxide reducing power.

The amounts of cane-sugar hydrolysed are expressed in percentages of the weight of the portions of the plant with which it was digested, and these are taken as expressions for the invertase in those portions.

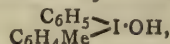
Check experiments made under similar conditions, (a) with cane-sugar solution saturated with chloroform, and (b) with chloroform water and portions of the same plants, showed that practically no cane-sugar is hydrolysed, and that the cupric oxide reducing power of the extract is a negligible quantity.

That organisms are not the cause of the hydrolysis of the cane-sugar was proved by "catching up" all the suspended matter in the chloroform water used in washing the portions of the plants, either by means of aluminium hydrate or paper pulp. The aluminium hydrate deposit and the paper pulp, which would contain all the suspended matter—and consequently any organisms present—when digested with similar cane-sugar solutions as in the experiments, gave no more cupric oxide reducing power than the cane-sugar solution and chloroform alone.

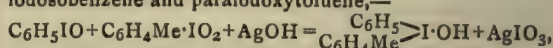
41. "Iodonium Compounds of the Type $IR^1R^2R^3$ and the Configuration of the Iodine Atom." By F. STANLEY KIPPING, Ph.D., D.Sc., F.R.S., and HAROLD PETERS.

It has been shown by Hartmann and Victor Meyer (*Ber.*, 1894, xxvii., 502, 1592) that diphenyliodonium hydroxide, $(C_6H_5)_2I\cdot OH$, is obtained when a mixture of iodosobenzene and iodoxybenzene is shaken with silver oxide and water; the authors have made use of this reaction for the preparation of iodonium bases containing different aromatic radicals.

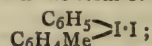
Phenylparatolyliodonium hydroxide,—



is formed, together with its iodate, from a mixture of iodosobenzene and paraiodoxytoluene,—



and is easily isolated in the form of its *iodide*,—

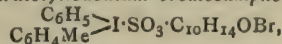


this salt crystallises from boiling water in small, almost colourless needles, and decomposes at about 153° .

A phenylparatolyliodonium iodide, identical in ordinary properties with the salt just mentioned, is obtained when a mixture of iodosoparatoluene and iodoxybenzene is treated with silver oxide and the product isolated as before.

The identity of these two preparations, if confirmed by further investigation, may be taken as showing that two of the three valencies of the iodine atom are symmetrically situated with respect to the third.

Attempts to resolve the phenylparatolyliodonium base into enantiomorphous components have so far been unsuccessful. When its iodide is treated with silver bromocamphor sulphonate in alcoholic solution, it is converted into *phenylparatolyliodonium bromocamphorsulphonate*,—



a compound which separates from aqueous alcohol in highly lustrous, well-defined crystals, which contain water of crystallisation, and have in consequence an indefinite melting point.

The same salt is obtained from the two iodides which have been prepared by the different methods stated above.

When this phenylparatolylidonium bromocamphorsulphonate is fractionally crystallized, the various deposits appear to be identical in ordinary and in optical properties; owing to the slight solubility of the salt in cold water, its specific rotation had to be determined in weak aqueous methyl alcohol, three different fractions giving $[\alpha]_D = +45^\circ$, $+45^\circ$, and $+47^\circ$ respectively.

The samples of salt used contained about 3.6 per cent of water, so that the molecular rotation of the anhydrous substance would be approximately $[M]_D = +283^\circ$; other experiments showed that the presence of methyl alcohol has little effect on the specific rotation, so that, since the molecular rotation of the acid is $[M]_D = +270^\circ$ in aqueous solution, it may be inferred that the idonium base is optically inactive in all three fractions; unless, therefore, the bromocamphorsulphonate is a partially racemic salt, it may be provisionally concluded that the three iodine valencies, to which the several radicles are attached, are arranged in one plane.

The further investigation of the various points raised in this preliminary note is in progress.

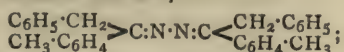
42. "Note on the Decomposition of Semicarbazones." By F. STANLEY KIPPING, Ph.D., D.Sc., F.R.S.

In working with various semicarbazones—as, for example, with those of dimethylketohexamethylene, ketotetrahydronaphthalene, ketophenoheptamethylene—it was noticed that a brisk evolution of gas usually occurred when such compounds were melted, but that little if any charring took place. It seemed, therefore, that the decomposition products might be easily isolated, and that their examination would show the nature of the change which had occurred.

The only reference in the literature relating to this subject seemed to be that of Scholtz (*Ser.*, 1896, xxix., 610), who, in attempting to prepare pyridazine derivatives, discovered that the semicarbazones of methylethyl ketone, and of other fatty ketones of low molecular weight, were decomposed on dry distillation into ketazines and hydrazodicarbonamide.

The author finds that a similar change occurs in the case of the semicarbazones of aromatic compounds; when benzaldehyde semicarbazone, for example, is heated at a temperature above its melting point, it gives an almost theoretical yield of the *azine*, $C_6H_5 \cdot CH:N \cdot N \cdot CH \cdot C_6H_5$, the nature of which was established by direct comparison with the product of the interaction of benzaldehyde and hydrazine.

This formation of azines by the decomposition of semicarbazones seems also to take place in aqueous solution; when, for example, benzylparatolyl ketone is heated on the water-bath with an aqueous alcoholic solution of semicarbazide hydrochloride and sodium acetate, it seems to be converted in the first place into a colourless semicarbazone in the usual manner, but on continued heating the latter gradually changes into a canary-yellow product which is doubtless the *azine*,—



the latter is readily soluble in chloroform, but only very sparingly so in hot alcohol, and separates from a mixture of these solvents in yellow needles melting at $172-173^\circ$.

It may be concluded from these experiments that the formation of azines from aromatic semicarbazones is also a fairly general reaction.

Preparation of Glycol.—L. Henry.—The author has examined the action of the caustic alkalis on diacetone. The best results were obtained with slaked lime, $Ca(OH)_2$; the lime (1 molecule) is added gradually to the diacetone, and the semi-solid mass which is formed is distilled in vacuo. In this manner 93 per cent of the theoretical return of glycol is obtained.—*R. Trav. Ch. P.-B.*, xviii., p. 221.

CORRESPONDENCE.

A PLEA FOR UNIFORMITY IN ARTIFICIAL MANURE ANALYSIS.

To the Editor of the Chemical News.

SIR.—The strange differences in the results of analysis of manures, as performed by the works chemists and those of the buyers, and between those again and the reference chemists, are a source of never ending annoyance to the chemical manure manufacturers.

What is the cause of these differences? Is it want of experience or care on the part of one or the other chemist? That may be so in some cases, but it is certain that these discrepancies are almost entirely due to the want of uniformity in the methods employed for the analyses.

For instance, the methods used for the estimation of the water-soluble phosphoric acid in the superphosphates are both numerous and very varied; and at the outset there is a great diversity of opinion as to the correct method for extracting it. The following modes of procedure are adopted by different chemists:—

(a) 1 grm. superphosphate dissolved by washing on the filter with cold water. (b) 1 grm. by boiling for ten minutes or half an hour, and finally washing with boiling water. (c) 1 grm. stirred or shaken for half an hour with cold water, decanted, boiled with a new portion of water, and finally washed with boiling water.

In these cases the whole filtrate is tested straight away, whilst in the following only aliquot parts are taken for testing, after the solutions have been filtered:—(d) 10 grms. dissolved in 500 c.c. cold water by shaking for half an hour in a shaking apparatus. (e) 20 grms. in 500 c.c. cold water for two hours, or over night; and finally (f) 2.5 grms. with 1000 c.c. water, &c.

Now the tests themselves are done in varying ways; there are:—(1) The molybdic acid method in different modifications; (2) the uranium acetate method; and (3) the citrate method with different modifications again as to the strength and the quantities to use.

I am not going to criticise these different methods as to whether they are more or less exact or not, as very often it resolves itself into a matter of personal opinion as to the correct method to pursue, and besides that, be they correct or not, the essential point is that they are actually in use, and that they show important differences in the results. I have often observed those over 2 per cent of tribasic phosphate of lime.

About the differences due to the various methods of extraction, I beg to mention that they are less marked or even nothing in fresh and well dissolved supers and in bone manures than in old stock, and in those manures much inclining to revert by lying, such as supers made from Tennessee phosphate.

Partly dissociation of the monobasic phosphate of lime, when dissolved in water—principally if the super is short in acid—into dibasic phosphate and free phosphoric acid, also a varying percentage of Al_2O_3 and Fe_2O_3 , may, to a certain extent, explain why some classes of manure are much more sensibly delicate as regards the method of extraction than others.

The following consideration may show how unreasonable and unpractical the use of divergent methods is:—

The value of a delivery of superphosphate is determined by two factors, the weight and the strength, the latter as found by chemical analysis, the unity for the weight being "1 ton," and for the strength "1 per cent tribasic phosphate of lime ($Ca_3[PO_4]_2$) soluble in water." But as different methods for testing the soluble phosphate may give in the same superphosphate different results, *i.e.*, may show a different number of units—and it is a fact, the differences are of distinct value for each two methods and each sample, and not accidental—those units arrived at by the different methods, say, for instance, "1 per cent tribasic phosphate of lime soluble in water (by cold

extraction)," and "1 per cent tribasic phosphate of lime soluble in water (by hot extraction)," cannot be of equivalent value, but must also be different. Therefore, using different methods for the same sample, means giving the strength (commercial value), of a superphosphate in different units; and if that is done by the works, buyers, and reference chemist it is in my opinion just as reasonable as if the three interested parties check the weight by a totally different standard; say, for instance, the works send out a delivery of, say, 10 tons (English), the buyer checks the delivery by metrical tons, and as those two would naturally get different results, a referee is asked to decide. But this one uses American (short) tons for weighing the questionable lot. Who could say that is just and reasonable?

In my opinion it is of the greatest interest to chemical manure manufacturers to seek for uniformity of the methods between themselves and the public chemists, and to lay down in this way for the strength of the manure a uniform standard, as already exists for the weight. Because when that is done the manufacturer will not run the risk of being found by the referee under the guarantee with his manures, and of damaging his commercial reputation thereby, although he makes them high enough to show 1 per cent or more over guarantee according to the test of his works chemist.

That has been recognised by the manufacturers of other countries, for instance of Germany, as their methods as published in the small pamphlet entitled "Methoden zur Untersuchung der Kuenstlichen Duingemittel—Verein Deutscher Duingerfabrikanten." (R. Gaertner's "Verlagsbuchhandlung H. Heyfelder," Berlin, S.W., Schönebergerstr. 26), agree in all essential points with those of the official "Versuchs und Controlstationen."

In one word then, "Uniformity of methods is the first condition for uniformity of the results."—I am, &c.,

W. JERWITZ, Ph.D.

31, Nottingham Street, off North Strand,
Dublin.

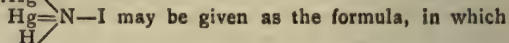
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 9, February 26, 1900.

Volume Composition of Hydrofluoric Acid.—Henri Moissan.—In a previous paper the author shows that hydrogen and fluorine combine in darkness without the application of any external energy. Hydrofluoric acid is formed with evolution of 38.6 cal. of heat. This method of formation of hydrofluoric acid is, however, too violent for good measurements to be taken, so another method was adopted by which a known volume of fluorine acts on water, and the volume of oxygen produced is measured, $\text{H}_2\text{O} + \text{F}_2 = 2\text{HF} + \text{O}$. The oxygen so produced was found to be strongly ozonised. As a result of a series of experiments, it was found that one volume of fluorine unites with an equal volume of hydrogen to give double the volume of gaseous hydrofluoric acid.

Use of Ferricyanides for Oxidation by means of Dehydrogenation. Oxidation of Camphor.—A. Etard.—Ferrocyanides and ferricyanides form, as is well known, numbers of characteristic precipitates with the alkaloids and other substances containing nitrogen, the action of primitive addition being evident in these cases. The example used for the author's experiments is camphor, and from his results he arrives at the following conclusions:—(1) The ferricyanides are the specific oxidisers; (2) they act more especially on nitrated bodies by dehydrogenation; (3) there are no strong and weak agents of oxidation, but the points of combination and of decomposition depend on the relative structure of the oxidising agent and the oxidised body.

Anhydrous Dimercurammonium Iodide, Amorphous and Crystalline.—Maurice François.—Weyl is said to have obtained anhydrous dimercurammonium iodide in a very unstable form by treating mercuric iodide with liquefied ammonium under pressure. Up to the present the dimercurammonium iodide obtained by the action of ammonia on mercuric iodide and on mercurdiammonium iodide was considered to be hydrated, the formula $\text{Hg}_2\text{NI} \cdot \text{H}_2\text{O}$ being given to this substance, or $\text{HO} \cdot \text{Hg} \begin{smallmatrix} \diagup \\ \text{N} \\ \diagdown \end{smallmatrix} \text{I}$ may be given as the formula, in which



HgOH is considered as a monatomic group. The investigation of this substance has led the author to believe that it is always anhydrous; the formula being Hg_2NI and the salt excessively stable. The preparation is effected by means of concentrated ammonia acting on mercurdiammonium iodide or on mercuric iodide, if the latter is pure and anhydrous and a sufficient volume of ammonia is used. It is quicker, however, to prepare the salt by the action of concentrated solutions of potash or soda on mercurdiammonium iodide—an action limited and reversible, like the preceding one.

Estimation of Ammonia and Nitrogen.—A. Villiers and E. Dumesnil.—The inaccuracy of acidimetric estimations in the presence of ammonia salts is well known. To estimate nitrogen the method of transformation into ammonia ought to give better results than the volume estimation of Dumas. The authors find, however, that it is often less exact, and they suggest a simple modification by which the weight of the ammonia or of the nitrogen may be determined with absolute accuracy. The volumetric estimation of ammonia is replaced by a gravimetric determination in the form of ammonium chlorhydrate. Even though the method seems to be longer, since it necessitates an evaporation and a desiccation, it is in reality a more practical and simple method than the volumetric one, since, when the desiccation is finished, there is but a single weighing, and the extra time of the estimation is largely compensated for by the perfect exactness of the results.

Chemical Equilibrium of a System in which Four Gaseous Bodies are present.—H. Pelabon.—This paper is unsuitable for abstraction.

MEETINGS FOR THE WEEK.

- MONDAY, 26th.—Society of Arts, 8. (Cantor Lectures). "Photography of Colour," by E. Sanger Shepherd.
TUESDAY, 27th.—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
WEDNESDAY, 28th.—Society of Arts, 8. "Leather for Bookbinding," by Douglas Cockerell.
THURSDAY, 29th.—Royal Institution, 3. "Equatorial East Africa and Mount Kenya," by H. J. Mackinder, M.A.
— Chemical, 3. Annual General Meeting. At 8.30, "Bunsen Memorial Lecture," by Sir Henry E. Roscoe, F.R.S.
— Society of Arts, 4.30. "The Cultivation, Manufacture, and Use of Indigo—Position of the Industry in India," by Christopher Rawson, F.I.C.
FRIDAY, 30th.—Royal Institution, 9. "Facts of Inheritance," by J. A. Thomson, M.A.
SATURDAY, 31st.—Royal Institution, 3. "Polarised Light," by The Rt. Hon. Lord Rayleigh, M.A., D.C.L., &c.

BENZOLE.

300 Tons Coke-oven Benzole wanted for delivery during present year.

Address, "H. Z., 3005," care of Rudolf Mosse, Hamburg.

Albumens, Glues, &c., and solutions for clarifying, polishing, waterproofing, stiffening, softening, thickening, &c.—G. KING, Benson St., Liverpool.

A Young Chemist, having good theoretical knowledge and many years' practical experience, and speaking three languages, seeks employment, preferably in the Colonies. References can be given.—Address letters to O. P. C., CHEMICAL News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

THE CHEMICAL NEWS.

VOL. LXXXI., No. 2105.

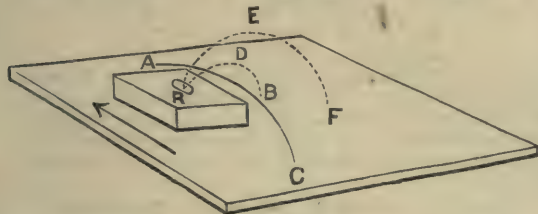
BECQUEREL RAYS.

CONFIRMATION OF THE MATERIALIST THEORY OF THE DEVIABLE RAYS OF RADIUM.

RADIUM has again occupied the post of honour during the last fortnight. After the discoveries of which we have recently written, a quiet time was to be expected; such, however, has not been the case, and far from diminishing in importance, the facts made known during these last few weeks surpass in novelty and interest all those of which the discovery has already excited such enthusiasm.

For some time we have been working in the dark, and were vainly endeavouring to find the point whence light would come. We already knew that the emission of radium did not agree with our ideas on ether waves; but the facts already known did not yet warrant us in believing that it was of a material nature. A decisive experiment of this kind, as we shall see immediately, has just been made by M. Curie; however, to properly understand and appreciate it, it is necessary to consider the question a little further back.

In a paper recently presented to the Academy, M. Becquerel has pointed out certain several remarkable facts with regard to the propagation of the emission of radium. The active substance was contained in a little recess, hollowed in a lead slab, *R* (see Figure), placed directly on the



Photographic plate acted on by radium *R*, contained in a recess hollowed in a lead slab placed on the plate. *R D B*, *R E F* are rays deviated by the magnetic field; *A B C* is an elliptical arc limiting the zone acted on by the most refrangible rays. The arrow shows the direction of the magnetic field.

photographic plate, and the whole was placed in a uniform magnetic field parallel to the plate. Under these conditions the impression due to the rays emitted from below upwards, and bent back on to the photographic plate by the action of the magnetic field, is limited on the side of its source by an elliptical arc, *A B C*, in the interior of which no photographic action can be observed, while such action can be seen diffused gradually towards the parts furthest distant from the source. The rays have thus described the arcs, *R D B* and *R E F*, of which the shortest are situated in the plane perpendicular to the direction of the field, while the oblique arcs have rays of much greater length.

The aspect alone of the photographic plate shows that the emission is complex, since the same field acts in a different manner on the various rays emanating from the source. But this complexity becomes still more evident if we interpose screens in the trajectory of the rays. Under these conditions the impression nearest to the source is suppressed, the line of light recedes, and gets further from the source the more the substance is absorbent. We thus see that the strongly curved rays are absorbed more than the others, without any other apparent selection, no matter what the screens are made of.

Now let us examine this characteristic from the point of the materialist theory of the rays, and let us suppose

that the particles emitted by the radium have different speeds.

We know that for a same quotient of mass by the charge, the product of the field by the rays of curvature is proportional to the speed.* Thus the particles which strike the plate the furthest from the source will be those possessing the greatest speed, and it is natural that they should also be the most penetrating.

This is a simple idea from which a presumption may result, but not a certainty. In fact other hypotheses could explain the same coincidence which can only be considered as an accessory proof. But the experiment of M. Curie gives us a proof of another order. He has placed beyond doubt the fact that the emission of radium charges bodies which receive it negatively, while the radium itself is charged positively.

This fact is of such importance, it throws such sudden light on the whole question, that the eminent physicists to whom we owe these marvellous discoveries would naturally wish to put it in evidence, and we believe they would have succeeded sooner had it not been for the extraordinary difficulties offered by the experiment. We do not propose to give it in detail, or to diminish the interest of the publication *in extenso* which belongs to M. and Mdme. Curie. We will only say that the extreme minuteness of the effects to be measured necessitated the most delicate apparatus, and that the method with piezoelectric quartz, of which M. and Mdme. Curie have made such constant and skilful use, alone could lead to positive results. But this is not all. The already known action of the new radiations was the principal obstacle to the success of the experiment. Radium placed at the mouth of a Faraday cylinder, while sending its own charged particles into the interior, created by that action a permanent conductor along their path, and provoked the immediate dissipation of the whole of the charges carried. It was therefore necessary to abandon this simple method, and to have recourse to a series of artifices, of which the most important consisted of enclosing the receiver in a double envelope, the first or outer one consisting of a metallic sheet connected to earth, while the second was isolated. A part of this double envelope was formed of thin leaves, permitting the radiation to reach the receiver.

In a second experiment, the radium itself was enclosed in the double envelope and discharged its negative charge to the exterior without compensation.

Only one interpretation seems still possible, at least for a portion of the emission of radium; this emission is composed of material particles carrying negative charges.

We might, at first sight, ask if the non-deviable rays are not a particular form of deviable rays. This does not seem to be the case, for the absorption they undergo would rather send them beyond the most deviable rays which have been met with. They are either of another kind, or they have been deprived of their charge of electricity. This latter idea is still admissible, and the singular manner in which these rays behave with regard to absorption, as we have pointed out in a recent article, would seem to confirm the idea.

Will this collection of well grounded ideas remove the last difficulties? To affirm this would be to proceed too quickly, since the cause of the bombardment is not yet apparent to us. In any case the first objection which comes to our minds, that of a necessary loss of mass of the radium, will not stand examination, for, as has been shown by M. Curie, the charges carried off are so feeble, that if we admit the same proportions as with cathodic rays, some millions of years would be required to remove 1 mgm. in the case of the most intense radiation that has yet been observed.

What can, however, be said with certainty, is that the new discoveries singularly limit the field for hypotheses, and by fixing the direction for research permit us to

* $\frac{m}{e} V = H \rho$, an equation established to explain the curvature of cathodic rays.

foresee a generalisation of great magnitude which will be of great attraction in the study of certain properties of matter to which in the last few years a large body of scientific men have turned.—*Revue Generale des Sciences*, No. 5, March 15, 1900.

NOTE ON THE PREPARATION OF METALLIC LITHIUM.

By LOUIS KAHLENBERG.

Up to the present time metallic lithium has been obtained by electrolysing lithium chloride in the molten state. The reason why this metal cannot be obtained from aqueous solutions by electrolysis is that it reacts with water, forming hydrogen and lithium hydroxide. It is evident that if a solvent for a lithium salt could be found upon which lithium does not act, the metal could be deposited from the solution by electrolysis, provided the solution proved to be an electrolyte.

Pyridine is a solvent of this kind. It will dissolve lithium chloride, and thus form a solution that conducts electricity. The electrical conductivity of such solutions is slight as compared with that of aqueous solutions. It has been determined by St. v. Laszczynski and St. v. Gorski (*Zeit. Electrochemie*, 1897, iv., p. 290). These investigators also attempted to precipitate the metal from the solution electrolytically. In their electrolytic cell they used a diaphragm in form of a porous cup, which greatly increased the internal resistance: and the cathode they employed was a short platinum wire 1 m.m. in diameter, so that the current density was relatively high. The anode consisted of a platinum foil. They used a pressure of 100 volts in their experiment in order to get a sufficient current. The result was that they obtained merely a black crust that contained metallic lithium.

I have found that lithium may be obtained in white metallic form from solutions of lithium chloride in pyridine by electrolysis at room temperatures. The method of operation is the simplest possible. It may be described as follows:—A concentrated solution of lithium chloride in pyridine is placed in a beaker into which dip a carbon plate (anode) and a bright iron plate or foil (cathode). Platinum or some other metal may, of course, also serve as cathode, though when used as anode a metal (even platinum) is apt to be attacked and some of its substance carried over to the cathode. No diaphragm is necessary. With a difference of potential of but 14 volts between the electrodes, a current of from 0.2 to 0.3 ampere per 100 sq. c.m. of cathode area will soon deposit a dense, well-adhering, silver-white, coating of metallic lithium. The deposit thus obtained possesses all the well-known physical and chemical properties of the metal.

Lithium, being an alkali metal that is not very plentiful in nature, has thus far not found use in practical life in the metallic form; nor are the indications at present such that it will be used in practice. Metallic lithium costs from 3 to 5 dollars per grm., and is used only for scientific purposes, mainly perhaps as a sample for exhibition in connection with lectures on chemistry.

By means of the method just described the metal can readily be obtained from the relatively cheap chloride in quantities sufficient for most scientific purposes. The method of preparation, as well as the properties of the metal, can thus easily be demonstrated to a class of students in a short time with simple means.

The method has not as yet been studied with a view of determining the conditions under which the yield is best, or to answer the question as to how large a quantity of the metal can thus be prepared economically. It may be stated, however, that the difficulties in obtaining lithium in quantity from this solution are in general those that are met in separating metals from their solutions in large quantities by means of the electric current.—*Wisconsin Engineer*, 1899, iii., 2.

SEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1899.*

By F. W. CLARKE.

THE year 1899 has not been remarkably prolific in determinations of atomic weight; and comparatively few investigations have been published. The data are given in the following pages, plus an account of two memoirs which appeared in 1898, but which reached this country only after the report for that year had been printed. These memoirs, by Vandenberghe on molybdenum, and by Kölle on cerium, were issued outside of the usual channels for chemical publication, and so seem to have escaped general notice hitherto.

Boron.

An elaborate memoir upon the atomic weight of boron has been published by Gautier (*Ann. Chim. Phys.*, [7], xviii., 352, Nov., 1899), who worked upon four different compounds. All weights were reduced to a vacuum, and all calculations were made with the atomic weights recommended a year ago by the Committee of the German Chemical Society.

First, sulphide of boron was decomposed by a dilute solution of caustic soda; the solution produced was then oxidised by means of bromine water, and the sulphur was precipitated and weighed as barium sulphate. The results obtained were as follows:—

Weight B ₂ S ₃ .	Weight BaSO ₄ .	Atomic weight.
0.2754	1.6312	11.032
0.3380	2.0004	11.081
0.3088	1.8300	11.000
0.2637	1.5614	11.050

Mean 11.041

The second compound studied was the carbide, B₆C. This was heated in chlorine gas to eliminate boron; the residual carbon was then weighed directly, and afterwards burned in oxygen to re-weigh as CO₂. The atomic weights given below were calculated from the weight of the carbon dioxide:—

Weight B ₆ C.	Weight C.	Weight CO ₂ .	Atomic weight.
0.2686	0.0429	0.1515	11.001
0.3268	0.0512	0.1844	10.994

Mean 10.997

With the third compound, boron tribromide, two series of experiments were made, representing two preparations. The bromide was in each analysis decomposed by water, special precautions being taken to avoid explosive reactions, and the bromine was finally precipitated and weighed as silver bromide. The data are subjoined:—

FIRST SERIES.

Weight BBr ₃ .	Weight AgBr.	Atomic weight.
3.1130	6.994	11.009
3.3334	7.490	10.981
3.7456	8.414	11.043
3.2780	7.364	11.032
4.2074	9.452	11.026

Mean 11.018

SECOND SERIES.

Weight BBr ₃ .	Weight AgBr.	Atomic weight.
3.3956	7.628	11.037
4.0295	9.052	11.032
3.7886	8.512	11.003
3.1711	7.124	11.026

Mean 11.025

* *Journal of the American Chemical Society*, vol. xxii., No. 2.

With boron trichloride the analyses were conducted precisely as in the case of the bromide, silver chloride being the final product weighed.

Weight BCl ₃ .	Weight AgCl.	Atomic weight.
2'6412	9'682	10'987
2'7920	10'234	11'000
2'4634	9'026	11'043
3'4489	12'640	11'013
2'2015	8'070	10'992
2'6957	9'878	11'030
Mean		11'011

The mean of the values obtained from the bromide and chloride series, 11'016, is the value which Gautier proposes to adopt.

Nitrogen.

Dean (CHEM. NEWS, lxxx., 279) has continued the investigation which was reported in 1898, relative to the atomic weight of nitrogen. The ratio studied is that between potassium bromide and silver cyanide, and the value finally found is N=14'031. Only an abstract of the paper has yet appeared.

Calcium.

A paper upon the atomic weight of calcium, by T. W. Richards, was read at the meeting of the American Association for the Advancement of Science in August, but has not, at the date of this report, been fully published. Five analyses of carefully purified calcium chloride were made to determine the ratio CaCl₂:2AgCl. Calculated with O=16 and Cl=35'455, the values found for Ca range from 40'121 to 40'130, the mean of all being 40'126.

Nickel.

The work of Richards and Cushman upon the atomic weight of nickel, noticed in the report of 1897, has been continued (*Proc. Amer. Acad.*, xxxiv., 327, February, 1899; CHEM. NEWS, lxxix., 163). The sublimed bromide was reduced in hydrogen, giving the ratio between bromine and the metal. The weights corrected for known impurities, and the values found are as follows:—

Weight NiBr ₃ .	Weight Ni.	Atomic weight.
2'83325	0'76081	58'705
3'21625	0'86358	58'696
2'31241	0'62094	58'703
2'87953	0'77330	58'710
2'29650	0'61679	58'719
2'98893	0'80272	58'714
5'51291	1'48056	58'716
2'24969	0'60415	58'710
Mean		58'709

All weights represent reductions to vacuum, and the antecedent values used in calculation are O=16 and Br=79'955. The complete agreement with the former determinations is almost startling. A full discussion of earlier determinations is given at the close of the paper, and it is shown that the work of Winkler and of Zimmermann is in accord with the new data.

Cobalt.

Just as in the case of nickel, Richards and Baxter have extended their observations upon cobalt (*Proc. Amer. Acad.*, xxxiv., 351, Feb., 1899; CHEM. NEWS, lxxix., 199), and now give three series of new determinations dependent upon the reduction of bromide to metal. In the first series, which is preliminary, a slight impurity is stated as "residue." In the other series corrected weights are given. The nature of the impurity, however, is fully discussed in the paper.

FIRST SERIES.

Weight CoBr ₃ .	Weight Co.	Residue.	Atomic weight.
5'59216	1'50873	0'00193	59'007
4'61944	1'24807	0'00426	58'996
3'75291	1'01713	0'00793	58'989
3'00645	0'81409	0'00510	59'007
Mean			59'000

SECOND SERIES.

Weight CoBr ₃ .	Weight Co.	Atomic weight.
5'32194	1'43428	58'996
7'50786	2'02321	58'989
2'32630	0'62677	58'973
7'44694	2'00736	59'011
Mean		58'992

THIRD SERIES.

Weight CoBr ₃ .	Weight Co.	Atomic weight.
5'10891	1'37721	59'016
6'41339	1'72850	58'999
6'59805	1'77876	59'021
3'02854	0'81606	58'982
Mean		59'004

The mean of the second and third series is 58'998, when O=16 and Br=79'955. Vacuum weights are given throughout.

In a still later paper (*Proc. Amer. Acad.*, xxxv., 61, August, 1899; CHEM. NEWS, lxxxii., 112) Richards and Baxter check their determinations of the atomic weight of cobalt by experiments upon the chloride and oxide. The chloride was reduced in hydrogen to metal, and the data obtained, after corrections for known impurities and reduction to a vacuum, were as follows:—

Weight CoCl ₂ .	Weight Co.	Atomic weight Co.
4'16483	1'89243	59'053
2'30512	1'04723	59'035
Mean		59'044

The reduction of cobalt monoxide in hydrogen was similarly effected, but with varying results depending upon differences in the conditions of the experiments.

First, three determinations, with vacuum weights, gave as follows:—

Weight CoO.	Weight Co.	Atomic weight Co.
7'04053	5'53779	58'962
6'69104	5'26312	58'974
7'83211	6'15963	58'927
Mean		58'954

These data, which are not sufficiently concordant among themselves or with the bromide determinations, probably indicate that the cobalt oxide contained some excess of oxygen. In a fourth experiment precautions were taken to avoid this difficulty, and 7'74242 grms. of oxide gave 6'09219 of cobalt, whence Co=59'068. In a fifth experiment, resembling the fourth, but with differences in detail, 10'58678 grms. of CoO gave 8'32611 of metal, corresponding to an atomic weight of Co=58'929.

The authors give elaborate particulars as to the circumstances under which each determination was made, and conclude that cobalt monoxide varies too widely in its composition to be suitable for exact measurements of atomic weight. The true value for cobalt undoubtedly lies between 58'93 and 59'07, the figure 58'995, obtained from the bromide, being the most probable.

(To be continued).

LIQUID HYDROGEN.*

By Professor DEWAR, M.A., LL.D., F.R.S., &c.

(Concluded from p. 139).

ON May 10, 1898, starting with hydrogen cooled to -205° , and under a pressure of 180 atmospheres, escaping continuously from the nozzle of a coil of pipe at the rate of about 10 to 15 cubic feet per minute, in a vacuum vessel doubly silvered and of special construction, all surrounded with a space kept below -200° , liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third vacuum vessel. In about five minutes 20 c.c. of liquid hydrogen were collected, when the hydrogen jet froze up, from the accumulation of air in the pipes frozen out from the impure hydrogen. The yield of liquid was about 1 per cent of the gas. The hydrogen in the liquid condition is clear and colourless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density appears at first sight to be in excess of the theoretical density, namely, 0.18 to 0.12, which we deduce respectively from the atomic volume of organic compounds, and the limiting density found by Amagat for hydrogen gas under infinite compression. A preliminary attempt, however, to weigh a small glass bulb in the liquid made the density only about 0.08, or half the theoretical. My old experiments on the density of hydrogen in palladium gave a value for the combined element of 0.62. Not having arrangements at hand to determine the boiling-point other than a thermo-junction which gave entirely fallacious results, experiments were made to prove the excessively low temperature of the boiling fluid. In the first place, if a long piece of glass tubing, sealed at one end and open to the air at the other, is cooled by immersing the closed end in the liquid hydrogen, the tube immediately fills where it is cooled with solid air. A small glass tube filled with liquid oxygen when cooled in liquid hydrogen is transformed into a bluish white solid. This is a proof that the boiling-point of hydrogen is much lower than any temperature previously reached by the use of liquid nitrogen evaporating *in vacuo*, seeing oxygen always remains liquid under such conditions. A first trial of putting liquid hydrogen under exhaustion gave no appearance of transition into the solid state. When the vacuum tube containing liquid hydrogen is immersed in liquid air, so that the external wall of the vacuum vessel is maintained at about -190° , the hydrogen is found to evaporate at a rate not far removed from that of liquid air from a similar vacuum vessel under the ordinary conditions of temperature. This leads me to the conclusion that, with proper isolation, it will be possible to manipulate liquid hydrogen as easily as liquid air.

The boiling-point of liquid hydrogen at atmospheric pressure in the first instance was determined by a *platinum resistance thermometer*. This was constructed of pure metal and had a resistance of 5.3 ohms at 0° C., which fell to about 0.1 ohm when the thermometer was immersed in liquid hydrogen. The reduction of this resistance to normal air thermometer degrees gave the boiling-points -238.2° and -238.9° respectively by two extrapolation methods, and -237° by a Dickson formula (see *Phil. Mag.*, 1898, xlv., 525). The boiling-point of the liquid seems therefore to be -238° C. or 35° absolute, and is thus about 5° higher than that obtained by Olszewski for the adiabatic expansion of the compressed gas, and about 8° higher than that deduced by Wroblewski from Van der Waal's equation. From these results it may be inferred that the critical point of hydrogen is about 50° absolute, and that the critical pressure will probably not exceed 15 atmospheres.

If we assume the resistance reduced to zero, then the

temperature registered by the electric thermometer ought to be -244° C. At the boiling-point of hydrogen, registered by the electric resistance thermometer, if the law correlating resistance and temperature can be pressed to its limits, a lowering of the boiling-point of hydrogen by 5° or 6° C. would therefore produce a condition of affairs in which the platinum would have no resistance, or would become a perfect conductor. Now we have every reason to believe that hydrogen, like other liquids, will boil at a lower temperature the lower the pressure under which it is volatilised. The question arises, How much lowering of the temperature can we practically anticipate? For this purpose we have the *boiling-point given by the hydrogen gas thermometer*, and critical data available, from which we can calculate an approximate vapour pressure formula, accepting 22° absolute as about the boiling-point, 33° absolute as the critical temperature, and 15.4 atmospheres as the critical pressure; then, as a first approximation—

$$\log. p = 6.410 - \frac{77.62}{T} \text{ m.m.} \quad (1).$$

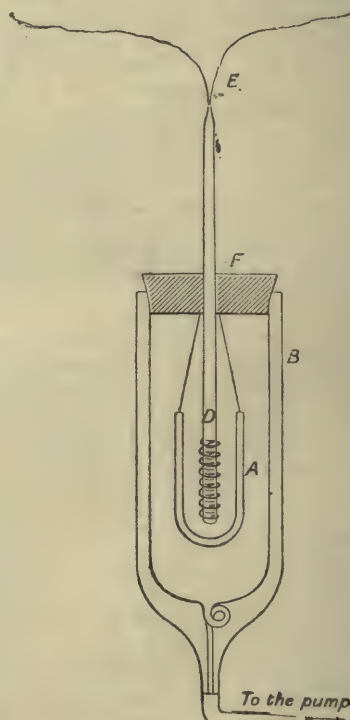


FIG. 2.

If, instead of using the critical pressure in the calculation, we assume the molecular latent heat of hydrogen to be proportional to the absolute boiling-point, then from a comparison with an expression of the same kind, which gives accurate results for oxygen tensions below one atmosphere, we can derive another expression for hydrogen vapour pressures, which ought to be applicable to boiling-points under reduced pressure.

The resulting formula is—

$$\log. p = 7.0808 - \frac{88}{T} \text{ m.m.} \quad (2).$$

Now formula (1) gives a boiling-point of 14.2° absolute under a pressure of 25 m.m., whereas the second equation (2) gives for the same pressure 15.4° absolute. As the absolute boiling-point under atmospheric pressure is about 22° , both expressions lead to the conclusion that ebullition under 25 m.m. pressure ought to reduce the boiling-point some 7° C. For some time experiments have been in

* A Lecture delivered at the Royal Institution, January 20, 1899.

progress with the object of determining the temperature of hydrogen boiling under about 25 m.m. pressure, by the use of the platinum thermometer; but the difficulties encountered have been great, and repeated failures very exasperating. The troubles arise from the conduction of heat by the leads; the small latent heat of hydrogen volume for volume as compared with liquid air; the inefficiency of heat isolation; and the strain on the thermometer brought about by solid air freezing on it and distorting the coil of wire. In many experiments, the result has been that all the liquid hydrogen has evaporated before the pressure was reduced to 25 m.m., or the thermometer was left imperfectly covered. The apparatus employed will be understood from Fig. 2. The liquid hydrogen collected in the vacuum vessel A was suspended in a larger vessel of the same kind B, which is so constructed that a spiral tube joins the inner and outer test-tubes of which B is made, thereby making an opening into the interior at C. The resistance thermometer D and leads E pass through a rubber cork F, and the exhaustion takes place through G. In this way the cold vapours are

perature and resistance for No. 7 thermometer is shown on the accompanying diagram (Fig. 3). As a matter of fact, however, this platinum thermometer was, when placed in liquid hydrogen, cooled at starting below its own temperature of perfect conductivity, so that no exhaustion was needed to bring it to this point. The question arises then as to what is the explanation of this result? Has the platinum resistance thermometer arrived at a limiting resistance about the boiling-point of hydrogen, so that at a lower temperature its changes in resistance become relatively small—the curve having become practically asymptotic to the axis of temperature? That is the most probable supposition, and it further explains the fact that the temperature of boiling hydrogen obtained by the linear extrapolation of the resistance temperature results in values that are not low enough.

As the molecular latent heats of liquids are proportional to their absolute boiling-points, the latent heat of liquid hydrogen will be about two-fifths that of liquid oxygen. It will be shown later, however, that we can reach from 14° to 15° absolute by the evaporation of liquid hydrogen

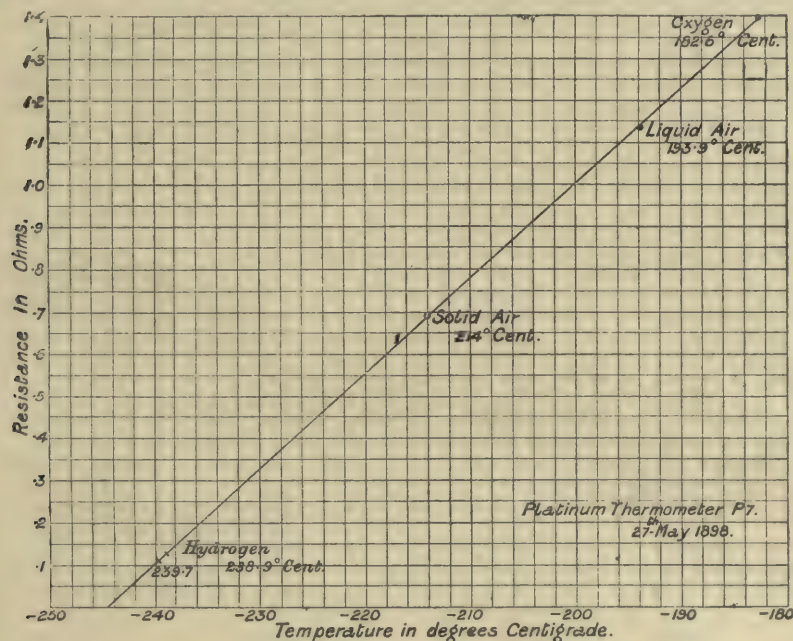


FIG. 3.

drawn over the outside of the hydrogen vacuum vessel, and this helps to isolate the liquid from the convective currents of gas. To effect proper isolation, the whole apparatus ought to be immersed in liquid air under exhaustion. Arrangements of this kind add to the complication, so in the first instance the liquid was used as described. The liquid hydrogen evaporated quietly and steadily under a diminished pressure of about 25 m.m. Naturally the liquid does not last long, so the resistance has to be taken quickly. Just before the reduction of pressure began, the resistance of the thermometer was 0.131 ohm. The result compares favourably with the former observation on the boiling-point, which gave a resistance of 0.129 ohm. On reducing the pressure, the resistance diminished to 0.114 ohm., and kept steady for some time. The lowest reading of resistance was 0.112 ohm. This value corresponds to $-239.1^{\circ}\text{C}.$, or only one degree lower on its own scale, than the boiling-point at atmospheric pressure, whereas the temperature ought to have been reduced at least 5° under the assumed exhaustion according to the gas thermometer scale. The position of the observation on the curve of the relation of tem-

perature and resistance for No. 7 thermometer is shown on the accompanying diagram (Fig. 3). As a matter of fact, however, this platinum thermometer was, when placed in liquid hydrogen, cooled at starting below its own temperature of perfect conductivity, so that no exhaustion was needed to bring it to this point. The question arises then as to what is the explanation of this result? Has the platinum resistance thermometer arrived at a limiting resistance about the boiling-point of hydrogen, so that at a lower temperature its changes in resistance become relatively small—the curve having become practically asymptotic to the axis of temperature? That is the most probable supposition, and it further explains the fact that the temperature of boiling hydrogen obtained by the linear extrapolation of the resistance temperature results in values that are not low enough.

The difficulties in liquefying hydrogen caused by the presence of air in the gas have been referred to (*Proc.*

Roy. Inst., 1898, xiv., 130), and later experiments had for their object the removal of this fruitful source of trouble. This is by no means an easy task, as quantities amounting to only a fraction of 1 per cent accumulate in the solid state, and eventually choke the nozzle of the apparatus, necessitating the abandonment of the operation. Later experiments enabled me to procure a larger supply of liquid hydrogen with which the determination of certain physical constants had been continued. The first observations made with a pure platinum resistance thermometer had given -238° as the boiling-point. A new thermometer, constructed of platinum from a different source, gave practically the same value. As these results might be affected by some constant error, the determination was checked by employing a thermometer constructed from an alloy of rhodium and platinum, containing 10 per cent of the former. Alloys had been shown by Prof. Fleming and the author to differ from pure metals in showing no sign of becoming perfect conductors at the absolute zero of temperature, and a study of the rhodium-platinum alloy had shown that the change in conductivity produced by cooling from 0° to the boiling-point of liquid air is regular and may be represented by a straight line. As determined by the rhodium-platinum thermometer, the boiling-point of hydrogen was found to be -246° or some 8° lower than the platinum thermometer gave. Two ways of explaining the discrepancy between the two values suggested themselves. Pure platinum, although its resistance may be represented by a straight line almost down to the solidifying point of air, shows signs of a departure from regularity at about this point, and the curve may become asymptotic at lower temperatures. On the other hand, the resistance of the rhodium-platinum alloy diminishes less rapidly at these lower temperatures and is much higher than that of pure platinum under similar conditions. It follows that its resistance curve, in all probability, deviates less from a straight line than is the case with platinum. Either cause would explain the differences observed, but the lower boiling-point (-246° or 27° absolute) seemed to be the more probable as it agreed very fairly with the value for the boiling-point calculated by the author from Wroblewski's results. As the use of other pure metals or alloys was not likely to lead to more satisfactory results, the problem had to be attacked in a different way, namely, by means of an "air" thermometer containing hydrogen under diminished pressure.

A first attempt has been made at determining the boiling-point by a constant volume hydrogen thermometer working under diminished pressure. This thermometer, which gave the boiling-point of oxygen as 90.5° absolute or -182.5° , gave for hydrogen 21° absolute or -252° . The three determinations that have been made are then as follows:—(1) pure platinum resistance thermometer, 35° absolute; (2) rhodium-platinum resistance thermometer, 27° absolute; (3) hydrogen thermometer, 21° absolute. From this it appears that the boiling-point of hydrogen is really lower than was anticipated, and must range between 20° and 22° absolute. Further experiments will be made with thermometers filled with hydrogen prepared from different sources. A hydrogen thermometer filled with the gas obtained from the evaporation of the liquid hydrogen itself must be employed.

The approximate density of liquid hydrogen at its boiling-point was found by measuring the volume of the gas obtained by evaporating 10 c.c. of the liquid, and is slightly less than 0.07, or about one-sixth that of liquid marsh-gas, which is the lightest liquid known. It is remarkable that, with so low a density, liquid hydrogen is so easily seen, has so well defined a meniscus, and can be so readily collected, and manipulated in vacuum vessels. As hydrogen occluded in palladium has a density of 0.62, it follows that it must be associated with the metal in some other state than that of liquefaction.

The atomic volume of liquid hydrogen at its boiling-point is about 14.3, the atomic volumes of liquid oxygen

and nitrogen being 13.7 and 16.6 respectively at their boiling-points. The weight of a litre of hydrogen gas at the boiling-point of the liquid is about the same as that of air at the ordinary temperature. The ratio of the density of hydrogen gas at the boiling-point to that of the liquid is approximately 1:60 as compared with a ratio of 1:255 in the case of oxygen under similar conditions.

The specific heat of hydrogen in the gaseous state and in hydrogenised palladium is 3.4, but may very probably be 6.4 in the liquid substance. Such a liquid would be unique in its properties; but as the volume of 1 grm. of liquid hydrogen is about 14–15 c.c., the specific heat per unit volume must be nearly 0.5, which is about that of liquid air. It is highly probable, therefore, that the remarkable properties of liquid hydrogen predicted by theory will prove to be less astonishing when they are compared with those of liquid air, volume for volume, at corresponding temperatures.

With hydrogen as a cooling agent we shall get to from 13° to 15° of the zero of absolute temperature, and its use will open up an entirely new field of scientific inquiry. Even so great a man as James Clerk Maxwell had doubts as to the possibility of ever liquefying hydrogen (see "Scientific Papers, ii., p. 412). He says "Similar phenomena occur in all the liquefiable gases. In other gases we are able to trace the existence of attractive force at ordinary pressures, though the compression has not yet been carried so far as to show any repulsive force. In hydrogen the repulsive force seems to prevail even at ordinary pressures. This gas has never been liquefied, and it is probable that it never will be liquefied, as the attractive force is so weak." In concluding his lectures on the non-metallic elements delivered at the Royal Institution in 1852, and published the following year, Faraday said (see Faraday's "Lectures on the Non-metallic Elements," pp. 292-3):—"There is reason to believe we should derive much information as to the intimate nature of these non-metallic elements, if we could succeed in obtaining hydrogen and nitrogen in the liquid and solid form. Many gases have been liquefied: the carbonic acid gas has been solidified, but hydrogen and nitrogen have resisted all our efforts of the kind. Hydrogen in many of its relations acts as though it were a metal: could it be obtained in a liquid or a solid condition, the doubt might be settled. This great problem, however, has yet to be solved, nor should we look with hopelessness on this solution when we reflect with wonder—and as I do almost with fear and trembling—on the powers of investigating the hidden qualities of these elements—of questioning them, making them disclose their secrets and tell their tales—given by the Almighty to man."

Faraday's expressed faith in the potentialities of experimental inquiry in 1852 has been justified forty-six years afterwards by the production of liquid hydrogen in the very laboratory in which all his epoch-making researches were executed. The "doubt" has now been settled; hydrogen does not possess in the liquid state the characteristics of a metal. No one can predict the properties of matter near the zero of temperature. Faraday liquefied chlorine in the year 1823. Sixty years afterwards Wroblewski and Olszewski produced liquid air, and now, after a fifteen years' interval, the last of the old permanent gases, hydrogen, appears as a static liquid. Considering that the step from the liquefaction of air to that of hydrogen is relatively as great in the thermodynamic sense as that from liquid chlorine to liquid air, the fact that the former result has been achieved in one-fourth the time needed to accomplish the latter proves the greatly accelerated pace of scientific progress in our time.

The efficient cultivation of this field of research depends on combination and assistance of an exceptional kind; but in the first instance money must be available, and the members of the Royal Institution deserve my especial gratitude for their handsome donations to the conduct of this research. Unfortunately its prosecution will demand a further large expenditure. It is my duty to acknow-

ledge that at an early stage of the inquiry the Hon. Company of Goldsmiths helped low-temperature investigation by a generous donation to the Research Fund.

During the whole course of the low-temperature work, carried out at the Royal Institution, the invaluable aid of Mr. Robert Lennox has been at my disposal, and it is not too much to say that, but for his engineering skill, manipulative ability, and loyal perseverance, the present successful issue might have been indefinitely delayed. My thanks are also due to Mr. J. W. Heath for valuable assistance in the conduct of the experiments.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, March 8th, 1900.

Professor THORPE, F.R.S., President, in the Chair.

PROFESSOR WARINGTON, F.R.S., delivered a Lecture on "*Recent Researches on Nitrification.*"

During recent years, the chief investigations on the character and properties of the nitrifying organisms have been carried out in Winogradsky's laboratory in St. Petersburg, none having been executed in this country. Formerly, investigators had been unable to obtain pure cultures of the organisms; their chemical characters had, however, been studied, as their capacity for growth in a purely mineral solution allowed of their separation from most of the other organisms in the soil. It had been found that the process of nitrification consisted of two distinct pieces of chemical work, effected by two agents, which could be separated from each other; by the first (the nitrous organism), ammonia was converted into a nitrite; by the second (the nitric organism), the nitrite was oxidised to nitrate. These facts were first ascertained at Rothamsted.

To isolate the nitrous organism from soil, Winogradsky commences by a series of cultures in an inorganic solution containing an ammonium salt, and the ash constituents of plant food. From this solution, cultivations on solid media are started. For some years, silica jelly was employed, but Oméliansky now prefers plates of magnesium-gypsum saturated with the mineral solution already mentioned. To isolate the nitric organism, the preliminary cultures are made in a solution containing sodium nitrite and ash constituents. As a solid medium, purified agar, with nitrite and ash constituents, is made use of. The fermentable constituents of the agar have been previously removed by Beyerinck's method.

Winogradsky has examined soils from many parts of the world. He finds but one nitrous and one nitric organism in any soil. The nitric organism is everywhere the same species. The nitrous organism may vary. In Europe, N. Africa, and parts of Asia, the same species occurs, with variations in size, and in tendency to adopt a zoogloeal or motile condition; the latter condition displays the greater chemical energy. The nitrous organism from Java is a distinct species, having an extraordinarily long flagellum. The organism from S. America and Australia is generally different; it is a giant coccus. A few other investigators have described different nitrifying organisms, but the evidence adduced has in some cases proved erroneous, and is in other cases as yet insufficient to warrant its acceptance.

Winogradsky had proved by quantitative experiments that the nitrous organism derives its carbon from carbonic acid; the nitric organism possesses the same power. As both organisms flourish in darkness, the energy necessary for the construction of organic matter out of carbon dioxide and water is apparently derived from the oxidation, respectively, of ammonia or a nitrite. Later experiments have shown that the carbonic acid is, in every case,

probably taken from a supercarbonate. The nutrition of the bacteria which exist with the nitrifying organisms in a mineral solution requires further study. Stutzer states that his hypomicrobium grows in a mineral solution, and needs carbonic acid for its nutrition, yet possesses no nitrifying power; its source of energy requires explanation.

The refusal of the nitrifying organisms to grow on gelatin, and on most organic media, is well known. Winogradsky and Oméliansky have lately studied the influence of various kinds of organic matter on the nitrifying process. The presence of 0.5 of glucose in 1000 of liquid is sufficient to retard the action of both the nitrous and nitric organism, while about 2 per 1000 entirely prevents nitrification. Glucose has thus as great an influence upon the nitrifying organisms as phenol has on ordinary bacteria. Of simpler forms of organic matter, as sodium acetate, a much larger quantity is required to hinder nitrification.

The influence of ammonia in preventing the action of the nitric organism is very remarkable; 5 parts per million was sufficient to retard its action, and 150 parts per million prevented it altogether, a proportion which is comparable with an effective dose of mercuric chloride. It seems, however, probable that an increase in the quantity and energy of the nitric organism enables it to bear a somewhat greater quantity of ammonia.

It appears from careful trials that the nitrifying organisms are without action upon nitrogenous organic matter; even methylamine is unaffected by them. For nitrification of organic matter to take place, the aid of other organisms is necessary to decompose it and bring the nitrogen into the form of ammonia. The behaviour of the nitrifying organisms towards organic matter and ammonia is of great practical importance.

The lecture was illustrated by lantern slides, and by a number of specimens of pure cultures on solid media, sent by Professor Winogradsky from St. Petersburg. The principal publications referred to will be found in *Trans. Chem. Soc.*, 1891, lix., 484; *Archives des Sciences Biologiques*, i. and vii.; *Cent. Bakt.*, 1899, ii., 652; *Mitt. Landw. Institute Breslau*, i., 75; ii., 197; *Comptes Rendus*, 1899, cxxviii., 566.

On the motion of Sir W. T. THISLETON-DYER, seconded by Dr. HUGO MÜLLER, a vote of thanks was passed to Professor Warington for his lecture.

Ordinary Meeting, March 15th, 1900.

Professor THORPE, F.R.S., President, in the Chair.

Messrs. A. H. Bennett, A. W. Harvey, and H. W. Cook were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Heinrich Rowland Beringer, 11, Dolcoath Road, Camborne; John Richard Brooke, 20, Aberdeen Park, Highbury, N.; Arthur Brand Chater, 65, Queen Street, Brisbane; Nicholas Cullinan, Risca, Monmouthshire; John Cussons, 4, Mount Pleasant, Portmadoc; William Donald, Saltcoats, Ayrshire; Frederic Richard Ellis, 15, Elton Road, Bishopstoke, Bristol; Thomas FitzGibbon, 1, Clyde Cottages, Ilford; James Herbert Haynes, 73, Brynland Avenue, Bishopston, Bristol; Thomas Lamb Lockhart, Johannesburg, Transvaal.

The following letter, addressed to the President, has been received from Professor van't Hoff, in acknowledgment of the congratulations sent to him by the Officers and Council on the occasion of the celebration, in December last, of the completion of the 25th year of his Doctorate:—

Charlottenburgh, 20th February, 1900.

MY DEAR COLLEAGUE,—Still engaged in answering the congratulations I received on the occasion of my Jubilee, I now come again to those from the Chemical Society of London, which reached me through the kind intervention

of you and Professor Dunstan. I pray that you will convey my feelings of gratitude to the Society, which has so recently admitted me as one of its Foreign Members.—I am, yours truly,

J. H. VAN'T HOFF.

Of the following papers, those marked * were read:—

*43. "*The Vapour Densities of Dried Mercury and Mercurous Chloride.*" By H. BRERETON BAKER, M.A.

The vapour density of ammonium chloride has already been shown to be normal when carefully purified and dried (*Trans.*, 1894, lxxv., 615; 1898, lxxiii., 425), pointing to the fact that moisture is necessary for the dissociation of this substance. Experiments have been tried with purified and dried mercurous chloride with the view of finding out if it behaved in a similar way when vaporised. The determinations were made with a specially devised modification of Victor Meyer's apparatus in an atmosphere of nitrogen at 448°. The mean of five determinations gave a vapour density of 217.4. A determination of the vapour density of the undried substance in the same apparatus gave 118.4. Dried mercurous chloride did not give gold amalgam when gold was heated in its vapour. Under the same conditions, the gold amalgam was obtained with the incompletely dried chloride. Very dry mercurous chloride therefore would seem to have the formula, Hg_2Cl_2 at 448°.

Similar experiments were made with carefully purified and dried mercury at 448°. The mean of three determinations in an atmosphere of nitrogen was 108.1, so that the molecule of dried mercury is probably monatomic at this temperature.

DISCUSSION.

Mr. D. HOWARD said that prolonged experience in the sublimation of large quantities of mercurous chloride had shown that the presence of vapour of water seemed to determine the corrosive action of the vapour on iron, and that the behaviour of the vapour of the chloride in the comparatively imperfect dryness obtainable on a large scale, suggested a true sublimation rather than dissociation.

Professor DEWAR remarked that it might interest the Society to know that Lord Rayleigh had recently found liquid air to be an effective desiccating agent as compared with phosphorus pentoxide, and that shortly the results of new determinations of the density of hydrogen thus dried would be communicated to the Royal Society.

Professor McLEOD pointed out that it would be interesting to know the quantity of water which would be sufficient to cause the complete dissociation of the heated mercurous chloride, for if the quantity were known it might be possible to ascertain the mechanism of the change.

*44. "*The Preparation of Pure Hydrobromic Acid.*" By A. SCOTT.

The author recommends the employment of sulphurous acid as a better and more convenient agent for preparing hydrobromic acid from bromine than amorphous phosphorus, even when purified from chlorides as Stas recommends. Almost all samples of phosphorus contain arsenic to a certain extent, and this, by the action of the bromine, becomes arsenious bromide which distils over with the hydrobromic acid, giving rise to arsenites and arsenates in the bromides prepared from acid made in this way.

By distillation two or three times, the hydrobromic acid is easily separated from the sulphuric acid formed at the same time, but it is always safer to add a little barium bromide before the final distillation. The purity of the acid was all that could be desired; this was shown by preparing from it some pure potassium bromide and titrating it against pure silver with all Stas's precautions, when its equivalent was found to be 119.099 ($Ag = 107.03$). Similar determinations with potassium bromide from hydrobromic acid prepared as recommended by Stas (*Euvres*, I., 842), and by J. P. Cooke (Squibb's process)

(*Proc. Amer. Acad.*, 1881, xvii., 31), gave 119.099 and 119.102 respectively. Stas's own number (mean of 14 experiments) is 119.095.

*45. "*A New Sulphide of Arsenic.*" By A. SCOTT.

When phosphorus containing (as it almost always does) small quantities of arsenic is oxidised by nitric acid and the solution boiled down, at a certain degree of concentration the liquid becomes brown, provided too much nitric acid has not been used. This brown colour, as has long been known, is due to the separation of metallic arsenic by the reducing action of the phosphorous acid present. If, before the concentration has been carried so far, the liquid be diluted and sulphur dioxide passed into it and then warmed, a yellow precipitate of arsenic trisulphide is obtained, caused by the reduction of the sulphurous acid to hydrogen sulphide by the phosphorous acid. This reaction may be used as a test for arsenates by adding a few drops of phosphorus trichloride to the solution, then some sulphurous acid, and warming, when the yellow precipitate is obtained at once.

If, however, these substances be allowed to react at ordinary temperatures, a dark brown precipitate is obtained which consists almost entirely of a new arsenic sulphide having the formula As_3S_5 . This may be freed from the small quantity of trisulphide usually formed at the same time by repeated treatment with ammonia solution into which a little hydrogen sulphide has been passed. This new sulphide is unattacked by ammonia, colourless ammonium sulphide, or carbon disulphide, but dissolves in yellow ammonium sulphide, and is attacked by potash solution, giving a dark brown substance exactly like that obtained by Berzelius by the action of potash solution on realgar.

*46. "*The Action of Iodine on Alkalies.*" By R. L. TAYLOR.

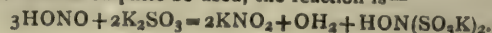
In the present paper, the author describes experiments using iodine in much stronger solutions—decinormal—sixty times the strength of the aqueous solution previously used by him (*Mem. Lit. and Phil. Soc. Manch.*, 1897, xli., viii.). Using Schwicker's method, he finds that if the requisite quantity (or more) of alkali is added to a decinormal solution of iodine and then a bicarbonate immediately added, from 88 to 94 per cent of the iodine is liberated, and therefore that amount of the iodine had reacted with the alkali to form hypiodite and iodide. By allowing different short intervals to elapse between the mixing of the alkali and iodine and the addition of the bicarbonate, he finds that the hypiodite decomposes with great rapidity even at the ordinary temperature. The stability of a hypiodite, in fact, depends upon its dilution, and this accounts for the definite results obtainable with very dilute solutions and the previous failures to obtain satisfactory evidence of the formation of hypiodite when strong solutions of iodine, or the solid itself, have been used.

The iodine used was in solution in potassium iodide, the only effect of using varying amounts of which was to vary the amount of alkali required to complete the reaction, as might indeed be surmised from the fact that the reaction is a reversible one.

The author concludes that the action of iodine upon alkalies in the cold is always the same in the first instance, namely, the formation of hypiodite and iodide, and that the hypiodite decomposes more or less rapidly, according to the concentration, into iodate and iodide.

*47. "*The Interaction between Sulphites and Nitrites.*" By EDWARD DIVERS and TAMEMASA HAGA.

The interaction of a nitrite with sulphurous acid or a sulphite, usually regarded as complicated, is really very simple. Nitrous acid, in the form of nitrous fumes, is entirely taken up by a solution of a pyrosulphite with the production of a two-thirds normal hydroxymidosulphate, thus $HONO + (KSO_3)_2SO_3K = HON(SO_3K)_2$. If the normal sulphite be used, the reaction is—



Sulphurous and nitrous acids themselves may be used to show the nature of this interaction, and to prove that neither the base of the nitrite nor the sulphite takes any part in the sulphonation. A sulphite does not act on a nitrite in presence of free alkali, and a pyrosulphite ceases to act when it has become the normal sulphite by its action upon the nitrite. The sulphonation of a nitrite requires always an acidic condition of the solution, and the authors maintain that, in every case, it is nitrous acid itself, rather than the nitrite taken, which suffers the sulphonation. Carbon dioxide or an acid carbonate causes a normal sulphite to act slowly upon a nitrite.

The statements of Claus, Berglund, and Raschig, that an alkaline hydroxide is produced in the sulphonation of a nitrite, is disproved by the authors, and shown to be due to a misconception of the facts observed.

Sulphur dioxide, passed into a solution of sodium or potassium nitrite and hydroxide, converts the latter into normal sulphite before sulphonation begins; pyrosulphite is then produced much faster than it can be consumed in sulphonating the nitrite, because of the retarding influence of the normal sulphite still present; and finally, when the quantity of the normal sulphite is sufficiently reduced, the pyrosulphite disappears faster than it is formed, leaving hydroximidodisulphate as the sole final product. If the normal carbonate be taken in place of the hydroxide, the sulphonation proceeds rapidly with the simultaneous production of acid carbonate and of sulphite over and above what is consumed in forming the hydroximidodisulphate, so long as any normal carbonate remains. Finally, the sulphite and acid carbonate are used up with the sulphur dioxide in sulphonating the last portions of the nitrous acid.

As it is nitrous acid itself which undergoes the sulphonation, the nitrite of any base should be capable of being used for the purpose, and the authors have tried with success not only the nitrites of sodium and potassium, but also those of ammonium, calcium, barium, zinc, mercury (ous), and silver.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 23rd, 1900.

Prof. W. E. AYRTON, F.R.S., Vice-President, in the Chair.

A PAPER ON "Some Experiments Illustrating Syntony" was read by Mr. A. E. SHAW.

The experiments described in this paper have been devised for the purpose of showing in a lecture room the principles of magnetic space telegraphy; the distance between the sending and receiving circuits being about 15 yards. A current flowing in a main circuit was interrupted by a tuning-fork of 100 vibrations per second, and a fraction of the current was passed through the sending coil. The sending coil was placed in series with a coil of adjustable self-induction, and the two coils were shunted with a condenser of variable capacity. By suitable adjustments an oscillation of frequency 400 could be maintained in the sending circuit. The receiving coil was in series with a variable self-induction and a variable capacity, and was tuned to respond to the waves given out by the primary. The current induced in the secondary coil was passed round a light drum fastened to a wire tuned to 400 vibrations per second. The drum was placed in a strong magnetic field, and the electrical oscillations caused mechanical vibrations of the drum. On to the drum was attached one carbon of a microphone, and the induced oscillations were thereby considerably magnified in the microphone circuit. This circuit was also arranged in the same way as the former, and by means of another microphone the vibrations were transferred to another circuit, where their intensity was sufficient to actuate the diaphragm of an ordinary telephone receiver to such an extent as to render the sound perfectly audible.

Mr. WATSON described some experiments which he had shown to illustrate syntony, both by obtaining galvanometer deflections and sparks in the secondary circuit.

Dr. LEHFELDT asked how the circuit was tuned when it contained both a variable capacity and a variable self-induction.

Mr. SHAW said that the values of the capacity and self-induction were connected with the vibration-frequency by a formula given by Dr. Lodge. Starting with a known capacity, the necessary self-induction was calculated and small alterations produced by means of an iron core.

Mr. SHAW then read a paper on "An Electrical Micrometer."

In this paper, the motion of the centre of a telephone diaphragm was measured by means of a system of levers and a spherometer screw. The screw, which had a pitch of 0.5 m.m. and a head divided into 500 parts, pressed against the long arm of an aluminium lever. The short arm of this lever pressed against the long arm of another, and so on through three levers. In this way any motion of the spherometer screw was transmitted to a fine platino-iridium point, close to a small platino-iridium disc fastened to the centre of the telephone diaphragm. Since the head of the spherometer could be accurately read to 0.1 of a division by means of a telescope, and since the system of levers minified any motion a hundred-fold, it follows that an accurately observable twist of the spherometer head corresponds to a movement of a millionth of a m.m., or 1 μ of the fine point. To test the action of the levers the point was removed, and a convex lens was substituted. This lens formed one of a system by means of which Newton's rings were produced and observed. By means of an optical experiment the author has found that 0.1 of a division on the graduated head equals 1.033 μ at the platino-iridium point. The point and the diaphragm then formed part of a circuit containing an ordinary telephone, and the levers were so adjusted that the point just touched the diaphragm. A sharp click was then heard in the telephone. A small current was then sent through the electromagnets of the original telephone, and the displacement of the diaphragm was measured by turning the spherometer screw until the point just touched it and a second click was heard. By carrying out a series of experiments of this description a curve has been drawn, showing the relation between current strength and diaphragm displacement. It is then interesting by extrapolation from the curve to find the movement which corresponds to the least audible sound. The author has done this, and finds that he cannot hear sounds if the amplitude is less than 0.37 μ . A motion of 50 μ gives comfortable sounds, 1000 μ uncomfortable sounds, and 5000 μ sounds unbearably loud. Throughout the experiments it was necessary to get rid of extraneous vibration by means of indiarubber balls and door-spring suspensions, and by working at night.

Prof. EVERETT expressed his interest in the delicacy of the system of measurement, and asked if the micrometer had been used to determine the form of the plate when vibrating.

Mr. PHILLIPS asked if experiments on the smallest sound audible had been made on different people, as it would be physiologically interesting to know if this minimum value were constant.

Mr. CAMPBELL asked if the sound was expected when heard.

Mr. SHAW said he had not conducted experiments on the form of the plate when vibrating, although he had investigated its law of damping. He said the small sounds were expected, and the limit varied.

The CHAIRMAN said he found it easy to rid galvanometers and electrometers from extraneous disturbance by placing them on a block of stone resting on a thickness of 3 or 4 feet of slag-wool contained in a hollow brick pillar.

The Society then adjourned until April 27th, when the meeting will be held at 8 o'clock in the Solar Physics Laboratory of the Royal College of Science.

NOTICES OF BOOKS.

Methods of Commercial and Industrial Analysis. ("Modes Opératoire des Essais du Commerce et de l'Industrie"). By L. CUNIASSE and R. ZWILLING. With a Preface by CH. GIRARD. Paris: Georges Carré and C. Naud. 1900. With 48 Illustrations. Pp. 302.

THIS volume is a collection of the methods now practised in commercial laboratories. In it we find described, in a clear and succinct manner, the analysis of water, air, alloys, and minerals; chlorometric and alkalimetric analysis; gold and silver assaying; the analysis of manures, fuels, and foods, gums and rubber, colouring matters, oils, paper and petroleum; in fact, of all the multifarious materials to be met with in trade and commerce. Tables of analytical coefficients are also given, which considerably lighten the work of calculating out results, and numerous references to original papers will be found throughout the work.

The book is well printed and bound, and will be found useful for reference, the table of contents and the index both being far better than is generally met with in French publications.

Volumetric Analysis. By JOHN B. COPPOCK, F.C.S., Inter. B.Sc. (Lond.), &c. London and New York: Whittaker and Co. 1899. Pp. 92.

THIS book is claimed to be specially adapted to the requirements of students entering for the Advanced Practical Chemistry Examinations of the Science and Art Department, also the Intermediate Science and Preliminary Scientific Examination of the University of London; it is primarily an appendage to the numerous excellent books already existing, and may be used as an introduction to volumetric analysis apart from the requirements of any particular examinations; in this respect it is more likely to be of real use. It contains an exhaustive collection of all the commoner determinations in which permanganate of potassium and standard solutions of acids and alkalis are used.

The use of potassium bichromate and silver nitrate is also included. The calculations are all worked out by simple rules of proportion, and the principles involved thoroughly explained.

We quite agree with the author that no part of practical chemistry gives the student a better conception of the quantitative meaning of a chemical equation than volumetric analysis.

Each chapter is provided with a number of questions, but we have not been able to find any special answers.

We must take exception to a note on the index page as a direct encouragement to laziness and scamping; it runs as follows:—"The student who wishes to restrict his work to the minimum required for success at his examination may ignore those determinations which are printed in italics in the index."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 10, March 5, 1900.

Preparation and Properties of a Perfluoride of Manganese.—Henri Moissan.—Fluorine attacks metallic manganese at ordinary temperatures. If the metal is in the form of a coarse powder, a layer of fluoride covers the surface and prevents further action, but when the

metal is finely powdered the heat of the reaction is enough to volatilise the fluoride formed. This reaction, however, results in no constant products, but when fluorine acts on manganese chloride—or better, on the iodide—an anhydrous perfluoride of manganese is formed corresponding to the formula Mn_2F_6 . This new compound is interesting, because a study of its reactions shows the molecule to be easily dissociable, and the excess of fluorine which it contains with respect to manganous fluoride acts as if it were free, $Mn_2F_6 = 2MnF_2 + F_2$. From this the author concludes that this perfluoride possesses a very great chemical activity. It allows of the preparation of new compounds which cannot be formed by direct union on account of the great evolution of heat which is produced in the reaction.

Definite Temperature Furnaces which can be Regulated at will.—Armand Gautier.—The author describes a furnace he has devised for his work on gaseous combinations at fixed temperatures. By this apparatus he was able to maintain any temperature from 150° to 1300° for an indefinite period.

Electric Charge due to the Deviable Radium Rays.—P. Curie and Mme. Curie.—It has been shown by previous experiments that the radium rays are deviated in a magnetic field in the same way as cathode rays. The authors now proceed to show that the deviable rays of radium are charged with negative electricity in the same way as cathode rays, only to a less degree. To prove the presence of a slight charge of electricity on the conductor which absorbs the rays, the metallic disc used as a conductor must be placed in a tube exhausted to a high vacuum, the tube being surrounded by a good solid dielectric. A drawing is given of the apparatus used. The current is measured by an electrometer. When the radiferous barium chloride formed a layer 2.5 sq. c.m. in surface and 0.2 c.m. thick, a current was obtained of about 10^{-11} amperes. Lead, copper, and zinc were successively used for the conducting disc, ebonite and paraffin for the dielectric, but in all cases the results were the same.

Preparation of Phosphides of Iron, Nickel, Cobalt, and Chromium.—Georges Maronneau.—The author was able to prepare phosphides of iron, nickel, cobalt, and chromium corresponding to the formulæ Fe_2P , Ni_2P , Co_2P , and CrP by the action of copper phosphide, melted in the electric furnace, on the respective metal. These compounds have been obtained previously by other methods, but their conditions of formation and of stability were, in the author's opinion, insufficiently established. The compounds prepared as above were found to be stable at the boiling-point of copper.

Eugenol, Safrol, and Propylpyrocatechin.—Raymond Delange.—Eugenol was shown by Ch. Moureu, by direct synthesis, to be an allylgaiacol with constitutional formula $CH_2=CH-CH_2-C_6H_3\begin{smallmatrix} OCH_3 \\ OH \end{smallmatrix}$. It would seem that, by simple demethylation, the unknown substance allylpyrocatechin would be formed. However, when treated with hydrobromic acid at 100° , methyl bromide is formed, the lateral chain being attacked at the same time. To simplify matters, the author proposed to obtain propylpyrocatechin, of which the saturated lateral chain is stable to agents of demethylation. He prepared this substance by two distinct methods, taking as a starting-point (1) eugenol and (2) safrol.

Diazotation of Safranin.—George F. Jaubert.—It has not been definitely established whether safranin gives one or more monodiazoic derivative. However this may be, the diazotation of safranin possesses a real importance, because, if safranin only gives one monodiazoic derivative, the formula of this colouring matter is incontestably that of a paraquinoid derivative. In the attempt to solve this problem, the author undertook a series of experiments on the diazotation of solutions of safranin, and finds that the safranin of commerce, diazotated under

the usual conditions of diazotation, gives but one mono-diazoic derivative.

Journal de Pharmacie et de Chimie,
Series 6, Vol. x., No. 12.

Preparation of Monocalcic Phosphate.—MM. Prunier and Jouve.—When bicalcic phosphate, $(\text{PO}_4)_2\text{Ca}_2\text{H}_2$, and orthophosphoric acid are added together in molecular proportion, with the necessary quantity of water, the whole dissolves. It seems natural to admit that the combination takes place according to the following equation: $(\text{PO}_4)_2\text{Ca}_2\text{H}_2 + 2\text{PO}_4\text{H}_3 = (\text{PO}_4)_2\text{CaH}_4$. In fact, it is the method described by Fourcroy and Vauquelin for the preparation of monocalcic phosphate. However, according as the experiment is conducted, the product formed changes its character; in fact, when working with the two halves of the same solution:—1. By rapidly evaporating the liquid we obtain a deposit of bicalcic phosphate mixed with a little monocalcic phosphate, if the evaporation is extremely rapid the deposit is formed entirely of bicalcic phosphate. 2. If, on the other hand, the action of heat is prolonged by boiling for an hour; for example, we only obtain a crystallisation of hydrated monocalcic phosphate. These peculiarities may be explained in several manners; the most satisfactory explanation appears to be, to admit that anhydrous monocalcic phosphate is less stable than the same salt hydrated; and that, on the other hand, its hydration is slowly effected. A solution of anhydrous monocalcic phosphate, submitted to rapid evaporation, will leave a deposit of hydrated bicalcic phosphate (this constitutes the most insoluble and the most stable body in acid medium). While, if the hydration has had time to take place, this salt being more stable, will not be sensibly dissociated, and the concentration goes on in the ordinary way. In any case, from the first moment of the solution of the product, the lime appears to exist entirely in the form of non-hydrated monocalcic phosphate, as this solution, precipitated by alcohol, gives only pure anhydrous monocalcic phosphate.

A New Method for the Estimation of Cyanide of Mercury.—E. Vincent.—Has been inserted in full (p. 122).

Speed and Limit of Etherification of Phosphoric Acid by Glycerin.—H. Imber and G. Belugou.—Whatever the temperature or state of hydration of the phosphoric acid, PO_4H_3 , nothing but monoalcoylphosphoric acid is formed, when this acid is acted on by glycerin. An equimolecular mixture of the two was made and analysed immediately, and also after the lapse of a variable number of hours. The mixture was kept at 15° . The results were:—

	Per cent of acid etherified.
Immediately.. .. .	19'33
After 2 hours	23'48
" 30 "	16'33
" 54 "	12'40
" 96 "	10'90

Thus the maximum coefficient of etherification was reached very quickly, while after that the quantity of ether diminished slowly. At 50° the results were very similar, but when the same experiment was repeated, at a temperature of 105° , the action was as follows:—

	Per cent of acid etherified.
Immediately.. .. .	22'74
After 1 hour	4'78
" 4 hours	12'40
" 5 "	14'70
" 22 "	31'97
" 28 "	32'72
" 45 "	43'12
" 75 "	42'87

These and other experiments showed that the return of glycerophosphoric acid depends essentially not only on the state of hydration of the acid and the temperature, but also on the time.

MEETINGS FOR THE WEEK.

- MONDAY, April 2nd.—Society of Arts, 4.30. "The Century in Our Colonies," by the Right Hon. Sir Charles Wentworth Dilke, Bart., M.P.
Society of Chemical Industry, 8. "The Manufacture of Caramel," by A. Gordon Salomon, A.R.S.M., F.I.C., F.C.S., and E. N. Goldie.
"Further Studies of the Furfuroids of Plant Tissues," by C. F. Cross, E. J. Bevan, and J. S. Remington.
Royal Institution, 5. General Monthly Meeting.
- TUESDAY, 3rd.—Royal Institution, 3. "The Structure and Classification of Fishes," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
Society of Arts, 8. "Process Engraving," by Carl Hentschel.
- WEDNESDAY, 4th.—Society of Arts, 8. "Cotton Supplies," by John A. Banister.
Society of Public Analysts, 8. "Note on the Influence of Temperature and Concentration on the Saline Constituents of Boiler Waters," by Cecil H. Cribb, B.Sc., F.I.C. "On an Improved Absorption Apparatus for Use in the Analysis of Essential Oils," by Alfred C. Chapman, F.I.C., and H. E. Burgess. "On the Composition of Danish Butters," by H. Faber. "The Composition of Milk and Milk Products," by H. Droop Richmond, F.I.C.
- THURSDAY, 5th.—Royal Institution, 3. "Equatorial East Africa and Mount Kenya," by H. J. Mackinder, M.A.
Chemical, 8. "The Liquefaction of a Gas by 'Self Cooling' " (a Lecture Experiment) and "Note on Partially Miscible Aqueous Inorganic Solutions," by G. S. Newth. "The Decomposition of Chlorates—II., Lead Chlorate," by W. H. Sodeau, B.Sc. "The Interaction of Mesityl Oxide and Ethyl Sodiomethylmalonate," by A. W. Crossley. "The Bromination of Benzene-azophenol," by J. T. Hewitt and W. G. Aston.
- FRIDAY, 6th.—Royal Institution, 9. "Solid Hydrogen," by Professor Dewar, M.A., LL.D., F.R.S.
- SATURDAY, 7th.—Royal Institution, 3. "Polarised Light," by The Rt. Hon. Lord Rayleigh, M.A., D.C.L., &c.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2106.

FLUORESCENCE OF CERTAIN METALLIC COMPOUNDS UNDER THE INFLUENCE OF RÖNTGEN AND BECQUEREL RAYS.

By PAUL BARY.

DURING the examination of the different salts which become luminous under the influence of X and Becquerel rays, I noticed that this property is acquired by certain salts of the following metals of the alkalis and alkaline earths:—Lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, and barium.

Experiments on the different salts of these metals permits of their classification in the following manner:—

	Fluorescent.	Non-fluorescent.
Lithium ..	Chloride.	Sulphate, phosphate.
Sodium ..	Chloride, sulphate, dithionate.	Carbonate, sulphide.
Potassium ..	Bromide, chloride, iodide, carbonate, sulphate.	Hydrate, nitrate, bi-sulphate, dithionate, sulphocyanide, ferricyanide.
Rubidium ..	Sulphate.	Bitartrate.
Caesium ..	Chloride.	—
Magnesium ..	Chloride, bromide.	Oxide, carbonate, sulphate, pyrophosphate, dimetallic phosphate, platino-cyanide.
Calcium ..	Chloride, fluoride, sulphide.	Sulphate.
Strontium ..	Oxide, chloride.	Nitrate, carbonate, phosphate.
Barium ..	Chloride, iodide, sulphide, sulphate, dithionate, formate, platino-cyanide.	Carbonate, nitrate, chlorate, sulphite, chromate, oxalate, ferrocyanide.

The above distinction between fluorescent and non-fluorescent salts is a little arbitrary, since, in certain cases, the fluorescence is so feeble that it can only be perceived by the observer who has been for some time in total darkness.

Of all the compounds of other metals which I have examined under similar conditions, none showed the phenomenon of fluorescence except phosphorescent salts of uranium. I also found by substituting for a Crookes tube, which I had previously used, a metallic vessel containing a radio-active substance (kindly placed at my disposal by M. and Mme. Curie), that all the bodies which showed fluorescence under the influence of X rays behaved in a similar manner with respect to Becquerel rays.

These results lead to the conclusion that the same class of bodies which give salts phosphorescent to light, give also compounds which become luminous under the influence of X and Becquerel rays. From this point of view, at least, these latter rays behave as if they were luminous rays of shorter wave length.

Concerning the permanent luminosity of radio-active barium salts prepared by M. and Mme. Curie, it is evident that this is due to the action of Becquerel rays on

the barium salt. Assuming, however, that the chemical properties of radium and barium are very similar, it appears probable that pure radium salts will prove to be fluorescent in the same manner as the other metals of this class.—*Comptes Rendus*, cxxx., No. 12, March 19, 1900.

THE VELOCITY OF THE IONS PRODUCED IN GASES BY RÖNTGEN RAYS.*

By JOHN ZELENY, B.Sc., B.A.,
Assistant Professor of Physics, University of Minnesota.

THE sum of the velocities with which the positive and the negative ions that are produced in gases by the Röntgen rays move when in a unit electric field has already been determined by an indirect method by E. Rutherford (*Phil. Mag.*, November, 1897). In the experiments here described the velocity was determined in a number of gases for the positive and negative ions separately, by comparing the ionic velocity directly with that of a stream of gas. The stream of gas was made to flow between two concentric cylinders, which were maintained at different potentials. By passing a narrow beam of Röntgen rays through the cylinders at right angles to their length, a narrow layer of ionised gas was produced. Due to the electric field between the two cylinders, the ions of this layer tended to move radially towards, or away from, the axis of the cylinders, but at the same time they were carried along by the stream of gas. Of the ions of this layer which travelled inwards, those that started from the inner surface of the outer cylinder were carried a distance X by the gas stream before they reached the surface of the inner cylinder.

This distance is dependent directly upon the mean velocity of the gas stream, and inversely upon the difference of potential between the two cylinders. For obtaining the difference of potential which must be used to allow the ions to be carried a certain distance along the tubes by the gas stream the inner cylinder was divided at some distance from the beam of rays into two parts, insulated from each other. That one of these parts which was not traversed by the rays was connected to a pair of quadrants of an electrometer, so that it was possible to tell when any ions reached it. A series of readings was taken for the charge reaching the electrometer in a given time for different values of the potential of the outer cylinder. From this was determined the value of this potential for which the ions starting from the outer edge of the ionised layer were just able to reach the juncture in the inner cylinder.

The ionic velocity in a unit electric field is given by the equation—

$$v = \frac{U(b^2 - a^2)}{2AX} \log_e \frac{b}{a},$$

where U is the mean velocity of the gas stream between the cylinders,

b is the inner radius of the outer cylinder,

a is the outer radius of the inner cylinder,

A is the potential of the outer cylinder, corresponding to—

X, the distance defined above.

To avoid the presence of vortices in the gas at the place where it was exposed to the rays, a sufficiently small velocity was used, and the gas was previously passed through a long portion of the cylinder to allow the motion to assume a steady state.

The disturbing influence upon the electric field between the cylinders of the free charges formed in the gas during the conduction was diminished by using weak rays. The fall of potential at the electrodes (*J. Zeleny, Camb. Phil. Soc. Proc.*, vol. x., Part I, p. 17) was also reduced by this means. For diminishing the amount of ionisation due to

* Abstract of a Paper read before the Royal Society, March 1, 1900.

Gas.	Ionic Velocities.				Ratio of negative to positive.	Temperature.
	Velocity in centimetres per second in a field of 1 volt per centimetre.		Velocity in centimetres per second in a field of 1 E.S.U. per centimetre.			
	Positive.	Negative.	Positive.	Negative.		
Air, dry	1'36	1'87	408	561	1'375	13'5° C.
Air, moist	1'37	1'51	411	453	1'100	14
Oxygen, dry	1'36	1'80	408	540	1'320	17
Oxygen, moist	1'29	1'52	387	456	1'180	16
Carbonic acid, dry	0'76	0'81	228	243	1'070	17'5
Carbonic acid, moist	0'82	0'75	246	225	0'915	17
Hydrogen, dry	6'70	7'95	2010	2385	1'190	20
Hydrogen, moist	5'30	5'60	1590	1680	1'050	20

the secondary radiation produced at the metal surface (J. Perrin, *Comptes Rendus*, cxxiv., p. 455), the cylinders were made of aluminium, for which metal the effect is the least.

The spreading of the ions due to diffusion produces an error, the amount of which increases with the time required for the ions to travel between the two cylinders.

The value of this time is found from the equation $T=X/U$, where X and U have the same significance as above.

The experimental values obtained for the velocity decreased as T increased, and from a series of results with different values of T the velocity could be obtained corresponding to $T=0$. Since in that case the effects of diffusion and similar causes disappear, this result was taken as the desired value of the ionic velocity.

For testing the accuracy of the method, in addition to using different values of U and X , changes were also made in the intensity of the rays, in the diameter of the internal cylinder, and in the metal which formed the inner surface of the outer cylinder.

Determinations were made with the gases when dry and when saturated with aqueous vapour, as the results were found to be different in the two cases. This is in agreement with the effect of moisture upon the coefficients of diffusion of the ions, as observed by J. S. Townsend (*Phil. Trans.*, A, vol. cxci, 1899). A summary of the results obtained is given in the accompanying table. The results are reduced to a pressure of 76 c.m. of mercury, but are not corrected for temperature, the effect of which is not known.

It is believed that in no case the error is greater than 5 per cent, while most of the observations indicate a considerably greater accuracy. It is observed that the presence of moisture always diminishes the velocity of the negative ions, and that in carbonic acid the velocity of the positive ions is at the same time markedly increased. The velocity of the negative ions is the greater in all of the cases except for moist carbonic acid. The ratios of the velocities of the ions previously determined for these gases by the writer (J. Zeleny, *Phil. Mag.*, July, 1898) were between those given above for the dry and for the moist gases, as the influence of moisture was unknown at that time, and the gases had not been dried.

E. Rutherford (*Phil. Mag.*, November, 1897) does not state whether he used dry gases in determining the sum of the velocities of the two ions produced by Röntgen rays; but his result for air (3'2 c.m. per second) agrees with the sum of the values separately obtained above for the two ions in dry air, while his values for oxygen (2'8 c.m. per second) and hydrogen (10'4 c.m. per second) correspond to those for the moist gases. His value for carbonic acid (2'15 c.m. per second) is higher than those here obtained. The value obtained by E. Rutherford (*Camb. Phil. Soc. Proc.*, vol. ix., Part VIII.) for the velocity of the negative ions produced in dry carbonic acid (0'78 c.m. per second) by the action of ultra-violet light, is quite near to that here obtained (0'81 c.m. per second) for the ions produced by Röntgen rays, but his values for dry air (1'4 c.m. per second) and dry hydrogen (3'9 c.m. per second) are considerably smaller.

In discharge from points, A. P. Chattock (*Phil. Mag.*, November, 1899) has obtained for the velocities of the positive and negative ions in dry air 413 and 540 c.m. per second respectively for a field of 1 E.S.U. per c.m., which values are quite close to those obtained here for the ions produced by Röntgen rays.

J. S. Townsend (*Phil. Trans.*, A, vol. cxci, 1899) has shown that from the coefficients of diffusion of the ions and from their velocities it is possible to compare the charges carried by the different ions, and also to compare them with those carried by the ions in the electrolysis of liquids. By using the velocities given above with the coefficients of diffusion determined by J. S. Townsend, the values of N_e are obtained, N being the number of molecules in 1 c.c. of the gas and e the charge carried by each ion. The results thus obtained for the moist gases, air, oxygen, and hydrogen, perhaps justify the statement that the charges carried by the positive and the negative ions are equal, and that the charge is the same for the different gases, and is equal to the charge carried by the hydrogen ion in the electrolysis of liquids.

The values of N_e obtained for the positive ions in these gases when dry are considerably larger than the above, while in carbonic acid all of the results are over 20 per cent smaller.

A NEW METHOD FOR THE DIRECT DETERMINATION OF ALUMINA IN PRESENCE OF IRON, MANGANESE, CALCIUM, AND MAGNESIUM.*

By WILLIAM H. HESS and E. D. CAMPBELL.

THE method most commonly used for the determination of alumina in presence of iron, manganese, calcium, magnesium, and phosphoric acid, is the indirect method in which the iron, alumina, and phosphoric acid are obtained together as a combined precipitate with ammonia. The alumina is taken as the difference obtained by deducting the weight of phosphorus pentoxide and ferric oxide as determined in separate samples. While the determinations of phosphoric acid, as well as the volumetric estimation of iron are satisfactory, an error may be introduced by careless ignition of the mixed oxides, since ferric oxide may be more or less converted to magnetic oxide (Fe_3O_4), with loss of oxygen; while in the calculations all the iron is figured as ferric oxide. Any error arising from careless ignition, from failure to perfectly wash the precipitate, or from an imperfect separation of other substances present as calcium, zinc, nickel, &c., goes to increase or decrease the percentage of alumina found.

Among the direct methods for determining alumina, the best known and most used are the alkali method and the thio sulphate method of Wöhler. Neither of these succeed satisfactorily when only traces of alumina are present with iron. Neither the potassium cyanide method nor the

* Contribution from the Laboratory of Analytical Chemistry, University of Michigan. From the *Journal of the American Chemical Society*, vol. xxi., No. 9.

basic nitrate method of Beilstein and Luther seem to have become popular. These methods, as well as many others that have been worked out, either require special expensive platinum apparatus or much attention to detail to obtain the correct conditions. In short, the present direct methods for estimating alumina are laborious, and too uncertain in their accuracy to pay for the heavy labour entailed, and consequently have not as yet displaced the simple though somewhat uncertain indirect method.

A method for the direct determination of alumina in presence of other substances commonly occurring with it, which is accurate, simple, and rapid, would seem to be of great practical value, especially to those chemists connected with the iron ore industry, with cement, and other clay industries, as well as in general mineral analysis.

While engaged in trying to modify the old alkali process so as to make it more satisfactory, experiments were carried on with a view of finding some reagent which would quantitatively precipitate alumina without precipitating iron. Recourse was taken to the organic bases for a suitable reagent for this purpose.

The well known ammonium base, phenylhydrazine, which has proved of such great value in establishing the chemistry of the sugars, was found to be the most satisfactory of the many organic bases tried for the precipitation of alumina. As a base it is somewhat weaker than ammonia. It precipitates aluminum from its solutions quantitatively as the hydroxide without a trace of the precipitate being re-dissolved in excess of the precipitant. Phenylhydrazine is, moreover, a strong reducing agent, quickly reducing iron from the ferric to the ferrous state, thus playing a double rôle of usefulness in the separation of iron from alumina.

Method of Analysis.

A convenient sample to be analysed is weighed out and obtained in solution preferably as the chloride in the usual way. To a convenient bulk of solution, 200 to 300 c.c. heated to near the boiling-point, dilute ammonia is added slowly as long as the precipitate formed just re-dissolves with readiness. A neutral, saturated solution of ammonium bisulphate* is added, drop by drop, with stirring to this hot and nearly neutral solution, until it becomes colourless, showing the complete reduction of the iron. To the hot solution now smelling strongly of sulphur dioxide, 1 or 2 c.c. of phenylhydrazine are added. If this amount of phenylhydrazine causes a permanent precipitate then a few drops more of phenylhydrazine are added to ensure complete precipitation of the alumina. If 1 to 2 c.c. of phenylhydrazine do not produce a permanent precipitate, it is economical, after adding this amount of phenylhydrazine, to add dilute ammonia carefully, drop by drop, to a just perceptible permanent precipitate, and then complete the precipitation by adding a few drops more of phenylhydrazine. The precipitate, consisting of aluminum hydroxide and aluminum phosphate, is filtered out on an ordinary filter and washed with warm water containing a small amount of phenylhydrazine bisulphite. This washing solution is prepared as follows: To a few c.c. of phenylhydrazine in a beaker, a saturated water solution of sulphur dioxide is added gradually until the precipitate of phenylhydrazine sulphite, which at first separates out in crystals, is re-dissolved to a yellow solution. If, after a few minutes, an odour of sulphur dioxide is perceptible, a few drops of phenylhydrazine are added to neutralise this excess of sulphurous acid. This concentrated solution of phenylhydrazine bisulphite, if well stopped, will keep indefinitely. 5 to 10 c.c. of this to 100 c.c. of water is an efficient strength of solution for washing the precipitate of alumina. The washing with this warm solution is con-

tinued until the washings give no test for iron with ammonium sulphide. A drop or two of phenylhydrazine is added to the filtrate with stirring to see if the precipitation has been complete. If chlorides of metals other than iron be present, the washing must be continued until the washings are free from chlorine. The presence of chlorides of volatile bases will do no harm in the ignition of alumina.

The precipitate together with the filter is placed in a platinum crucible, dried, and the filter charred at a low temperature. After the filter is completely burned, the ignition is continued at a bright red heat to constant weight. Care is taken to weigh quickly with the cover on the crucible, since both the phosphate and oxide of aluminum are very hygroscopic. A second ignition and weighing is always necessary. This precipitate of alumina carries all the phosphorus pentoxide so that the weight of alumina is found by subtracting the weight of phosphorus pentoxide found in a separate sample.

Chromium is quantitatively precipitated by phenylhydrazine, and may thus be separated from iron with great readiness. Neither calcium, magnesium, manganese, cobalt, or nickel is precipitated.

Gravimetric Method for Iron.

If a gravimetric estimation of the iron is desired, it has been found to be most expedient to add ammonium sulphide to the filtrate in case there is no other metal present that will be precipitated by this reagent. The sulphide of iron thus formed is filtered out, and without washing is re-dissolved in dilute hydrochloric acid. From this hydrochloric acid solution the iron is estimated in the usual way with ammonia after oxidation with nitric acid. It may under some circumstances be desirable to separate the iron and alumina by means of ammonia or as basic acetate, to get rid of other metals before attempting their specific separation by means of phenylhydrazine.

Separation and Estimation of Phosphoric Acid.

Since the aluminum hydroxide precipitated with phenylhydrazine carries all the phosphorus pentoxide with it that is present in the solution, this method may be conveniently used for its separation. If the alumina present in the mineral is not sufficient to carry all the phosphoric acid as the normal phosphate, an excess of a known solution of aluminum chloride is added. The alumina is then separated by the above method. If only the phosphoric acid is desired, this precipitate may be dissolved in nitric acid and the phosphoric acid may be determined in the usual way. Or the precipitate may be ignited and weighed, thus giving the combined weight of alumina added, of alumina in the mineral, and of phosphoric acid in the mineral.

Results on Known Mixtures.

Mixtures were made by Prof. Campbell's private assistant which were strictly unknown to the operator, and were subjected to the above method of analysis with results as recorded in the following table:—

	Weight of iron taken. Grm.	Al ₂ O ₃ taken. Grm.	P ₂ O taken. Grm.	P ₂ O ₅ +Al ₂ O ₃ taken. Grm.	P ₂ O ₅ and Al ₂ O ₃ found. Grm.	Gain or loss. Grm.
1.	0.7023	0.00664	0.00077	0.000741	0.000735	0.00006
2.	0.2020	0.1343	0.00022	0.13452	0.1343	0.00022
3.	0.059934	0.0105	0.00576	0.01581	0.0162	0.00039
4.	0.3339	0.0966	0.01072	0.10732	0.1066	0.00072
5.	0.6604	0.030	0.00577	0.03577	0.03570	0.00007
6.	0.551	0.05152	0.01073	0.06225	0.06220	0.00005
7.	0.527	0.0219	0.01073	0.03263	0.0330	0.00037
8.	0.564	0.0644	0.00822	0.07262	0.0719	0.00072

* This solution of ammonium bisulphite is made by passing sulphur dioxide into a cooled solution of ammonia (1:1) until the solution becomes yellow. It serves the purpose here, not only of reducing the iron, but the excess of sulphurous acid unites with the phenylhydrazine added, to form a salt which acts as a most efficient agent for keeping the iron reduced and thus prevents its precipitation with the alumina.

A solution was prepared by dissolving 1 gram. of calcium carbonate, 0.200 gram. magnesium carbonate, 0.571 gram. of ferric oxide, and 1 gram. of manganous chloride in hydrochloric acid. To this solution, 0.09016 gram. aluminum

oxide and 0.05234 grm. of phosphorus pentoxide was added. The combined weight of alumina and phosphorus pentoxide taken was therefore 0.1425 grm. The weight found was 0.1428 grm.

SEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1899.*

By F. W. CLARKE.

(Concluded from p. 147).

Molybdenum.

In 1897 the Belgian Academy of Sciences awarded a special Stas prize to M. Ad. Vandenberghe for his determination of the atomic weight of molybdenum. The memoir has recently been published (*Acad. Roy. des Sciences, Mémoires Couronnés*, 4to Series, Tome lvi., 1898), and the data are now available.

Vandenberghe starts out with molybdenum dibromide, scrupulously purified. From this he obtains metallic molybdenum, by careful reduction in hydrogen at a white heat. The atomic weight determinations are made by the oxidation of Mo to MoO₃, by means of pure nitric acid. The product was finally dried at a temperature of from 350° to 400°, and cooled in a current of oxygen. The data obtained are as follows:—

Weight Mo.	Weight MoO ₃ .	Atomic weight.
0.7143	1.0711	95.851
0.3453	0.5177	95.899
0.9693	1.4533	95.889
0.5089	0.7631	95.854
1.7219	2.5820	95.855
4.2597	6.3872	95.869

Reducing all weights to a vacuum, the final value becomes 95.829, when O=15.96. If O=16, Mo=96.069. If O=15.88, then Mo=95.349. This value is very near that found by Smith and Maas, by an entirely different method, but rather higher than that given by Seubert and Pollard. For all practical purposes the value Mo=96 may be assumed.

Tungsten.

Two investigations relative to the atomic weight of tungsten have been published from the laboratory of the University of Pennsylvania. The first one, by G. E. Thomas (*Journ. Am. Chem. Soc.*, xxi., 373, April, 1899), contains a record of experiments upon WO₃ and Na₂WO₄.2H₂O. The reduction of oxide to metal, and the reverse process of oxidation, gave figures ranging from 183.51 to 184.22 for the atomic weight of tungsten, and work along this line was discontinued. With sodium tungstate three series of dehydration experiments were made, giving the ratio between water and the anhydrous salt as the measure from which to calculate. These results also were discordant, and Thomas discards the method as unsuited to accurate determinations. The object of the paper seems to be negative, and to show that neither method employed is adequate to its purpose.

The second paper, by Professor Smith, contains a section by W. L. Hardin (*Journ. Am. Chem. Soc.*, xxi., 1017, November, 1899), of similar purport to that of Thomas. Experiments were made upon the oxide, the oxychloride, barium meta-tungstate, and the precipitation of silver by metallic tungsten, and each method was found to be defective. Discordant results were obtained in each set of trials. The mean of all experiments upon the reduction of WO₃ and the oxidation of tungsten give approximately the value W=184. This value Hardin

thinks it best to accept until more conclusive determinations shall have been made.

Cerium.

Kölle's dissertation ("Beiträge zur Kenntniss des Cers," Doctoral Dissertation by Gotthold Kölle, Zurich, 1898) upon this element deals partly with its atomic weight and partly with other matters. His material was obtained from cerite, and was purified with extreme care. Iodometric determinations of cerium salts gave, invariably, results which were too high, and which led him to believe that the source of error was in the accepted atomic weight of cerium—an essential factor in his calculations.

Accordingly, new determinations of atomic weight were made by the standard method, namely, the ignition of cerium sulphate to cerium dioxide. Cerium chloride prepared from the oxide was spectroscopically examined and found to be free from other metals. The atomic weight data are as follows, computed with O=16.

Weight Ce ₂ (SO ₄) ₃ .	Weight CeO ₂ .	Per cent CeO ₂ .	Atomic weight.
1.84760	1.11648	60.429	139.11
1.16074	0.70078	60.331	138.78
1.53599	0.92722	60.366	138.73
0.97196	0.58661	60.353	138.64
1.40374	0.84760	60.384	138.84
1.75492	1.05956	60.377	138.80
1.53784	0.92853	60.379	138.82
1.64233	0.99150	60.372	138.76

Mean . . . 138.81

This value is lower than any of the later determinations, but agrees nearly with that of Wolf. Like Wolf, and like some other recent investigators, Kölle obtained a white ceric oxide, and he regards the coloured preparations of former researches as evidently impure. Furthermore, iodometric estimations made on known quantities of ceric oxide gave good results when the new atomic weight was used in calculation, but excesses of 0.8 per cent when Brauner's or Robinson's value was employed. So far as present evidence goes, there is a presumption in favour of Kölle's determination.

Palladium.

Hardin's research (*Journ. Am. Chem. Soc.*, xxi., 943, November, 1899) upon the atomic weight of palladium is based upon the reduction of certain compounds in hydrogen. Neither of the salts studied had been previously applied to determinations of this character, and the results obtained are therefore of special value. They are, moreover, very concordant, and seem to be more nearly conclusive than any determinations previously made. All weights were reduced to a vacuum, and the calculations are based upon atomic weights given in the table of your committee for 1898.

First, diphenyl-pallad-diammonium chloride was studied. After reduction, the metal was heated in air to burn off possible free carbon, then re-heated in hydrogen, and cooled in air to prevent occlusion of the former gas.

Weight of salt.	Weight Pd.	Atomic weight.
0.98480	0.28953	107.06
1.10000	0.32310	106.92
1.08220	0.30210	106.96
1.19230	0.35040	107.00
1.40550	0.41300	106.98
1.26000	0.37040	107.04
2.25510	0.66310	107.08

Mean . . . 107.006

The second series of determinations was made upon diphenyl-pallad-diammonium bromide, with the following results:—

* *Journal of the American Chemical Society*, vol. xxii., No. 2.

Weight of salt.	Weight Pd.	Atomic weight.
0.88567	0.20917	107.01
1.31280	0.31000	106.99
1.50465	0.35540	107.03
2.01635	0.47635	107.05
2.92300	0.69080	107.10

Mean 107.036

Finally, ammonium-palladium bromide was studied, giving four more determinations:—

Weight of salt.	Weight Pd.	Atomic weight.
0.77886	0.18006	107.03
1.53109	0.35381	106.96
2.75168	0.63614	107.03
1.88136	0.43478	106.98

Mean 107.00

The mean of all three series, when O=16, is 107.014; 107, then, may be taken as the most probable value for the atomic weight of palladium.

Radium.

Madame Curie (*Comptes Rendus*, cxxix., No. 20; *CHEM NEWS*, lxxx., 281), having prepared a large quantity of radiferous barium chloride, has determined the chlorine in several fractions of the material, and so ascertained the atomic weight of the metal contained in it. Three determinations gave for this atomic weight:—

140.0
140.9
145.8

Hence the atomic weight of radium is higher than that of barium, although its true value is still unknown.

The Electro-chemical Equivalents of Copper and Silver.

This subject has been re-investigated somewhat elaborately by Richards, Collins, and Heimrod (*Proc. Amer. Acad.*, xxxv., 123, December, 1899). First, copper was precipitated in comparison of the silver and copper voltameters, under varying conditions as to temperature, character of solution, and size of plates, and the results are summarised as follows for the atomic weight of copper, when Ag=107.93:—

Large plates cupric solutions, t. 20°	Cu=63.47
" " " " t. 0°	63.525
Small " " " t. 0°	63.547
Medium " cuprous " t. 0°	63.573
" " " " t. 60°	63.615
Corrected results from cupric solutions	Cu=63.563

a value 0.041 lower than that determined by chemical processes.

A study of the silver voltmeter by itself showed that it gives results which are too high by about 0.081 per cent. Correcting the atomic weight of copper in accordance with this observation, the true value is found to lie between 63.598 and 63.615. The value previously established by Richards was 63.604, a confirmation of the present work, which is to be continued.

Table of Atomic Weights.

In the following table of atomic weights your committee give first its own set of values, based upon both fundamental standards; next is given Richards's table, revised for 1899; and, finally, that of the German Chemical Society. The values in the German table are rounded off to convenient approximations for practical use; those of Richards give the nearest significant figure, and the latter policy, which is wise, has also been adopted by your committee. There are, however, slight differences of opinion in some cases as to where the nearest significant decimal place really is. Hardin's work on cerium and tungsten, and Külle's research on cerium, have led to the only notable changes from last year,

		Clarke.		Richards.	German.
		H = 1.	O = 16.		
Aluminum ..	26.9	27.1	27.1	27.1	27.1
Antimony ..	119.5	120.4	120.0	120.0	120.0
Argon ..	?	?	39.9?	40.	40.
Arsenic ..	74.45	75.0	75.0	75.	75.
Barium ..	136.4	137.40	137.43	137.4	137.4
Bismuth ..	206.5	208.1	208.0	208.5	208.5
Boron ..	10.9	11.0	10.95	11.	11.
Bromine ..	79.34	79.95	79.955	79.96	79.96
Cadmium ..	111.55	112.4	112.3	112.	112.
Cæsium ..	131.9	132.9	132.9	133.	133.
Calcium ..	39.8	40.1	40.1	40.	40.
Carbon ..	11.9	12.0	12.0001	12.00	12.00
Cerium ..	138.0	139.0	140.	140.	140.
Chlorine ..	35.18	35.45	35.455	35.45	35.45
Chromium ..	51.7	52.1	52.14	52.1	52.1
Cobalt ..	58.55	59.00	59.00	59.	59.
Columbium ..	93.0	93.7	94.	94.	94.
Copper ..	63.1	63.6	63.60	63.6	63.6
Erbium ..	164.7	166.0	166.	166.	166.
Fluorine ..	18.9	19.05	19.05	19.	19.
Gadolinium ..	155.8	157.0	156.?	—	—
Gallium ..	69.5	70.0	70.0	70.	70.
Germanium ..	71.9	72.5	72.5	72.	72.
Glucinum ..	9.0	9.1	9.1	9.1	9.1
Gold ..	195.7	197.2	197.3	197.2	197.2
Helium ..	?	?	4.0?	4.	4.
Hydrogen ..	1.000	1.008	1.0075	1.01	1.01
Indium ..	113.1	114.0	114.	114.	114.
Iodine ..	126.89	126.85	126.85	126.85	126.85
Iridium ..	191.7	193.1	193.0	193.	193.
Iron ..	55.6	56.0	56.0	56.	56.
Lanthanum ..	137.6	138.6	138.5	138.	138.
Lead ..	205.36	206.92	206.92	206.9	206.9
Lithium ..	6.97	7.03	7.03	7.03	7.03
Magnesium ..	24.1	24.3	24.36	24.36	24.36
Manganese ..	54.6	55.0	55.02	55.	55.
Mercury ..	198.50	200.0	200.0	200.3	200.3
Molybdenum ..	95.3	96.0	96.0	96.	96.
Neodymium ..	142.5	143.6	143.6	144.	144.
Nickel ..	58.25	58.70	58.70	58.7	58.7
Nitrogen ..	13.93	14.04	14.045	14.04	14.04
Osmium ..	189.6	191.0	190.8	191.	191.
Oxygen ..	15.88	16.000	16.0000	16.00	16.00
Palladium ..	106.2	107.0	106.5	106.	106.
Phosphorus ..	30.75	31.0	31.0	31.	31.
Platinum ..	193.4	194.9	195.2	194.8	194.8
Potassium ..	38.82	39.11	39.140	39.15	39.15
Praseodymium ..	139.4	140.5	140.5	140.	140.
Rhodium ..	102.2	103.0	103.0	103.0	103.0
Rubidium ..	84.75	85.4	85.44	85.4	85.4
Ruthenium ..	100.9	101.7	101.7	101.7	101.7
Samarium ..	149.2	150.3	150.0	150.	150.
Scandium ..	43.8	44.1	44.	44.1	44.1
Selenium ..	78.6	79.2	79.2	79.1	79.1
Silicon ..	28.2	28.4	28.4	28.4	28.4
Silver ..	107.11	107.92	107.930	107.93	107.93
Sodium ..	22.88	23.05	23.050	23.05	23.05
Strontium ..	86.95	87.60	87.68	87.6	87.6
Sulphur ..	31.83	32.07	32.065	32.06	32.06
Tantalum ..	181.5	182.8	183.	183.	183.
Tellurium ..	126.5	127.5?	127.5?	127.	127.
Terbium ..	158.8	160.	160.	—	—
Thallium ..	202.61	204.15	204.15	204.1	204.1
Thorium ..	230.8	232.6	233.	232.	232.
Thulium ..	169.4	170.7	170.?	—	—
Tin ..	118.1	119.0	119.0	118.5	118.5
Titanium ..	47.8	48.15	48.17	48.1	48.1
Tungsten ..	182.6	184.	184.4	184.	184.
Uranium ..	237.8	239.6	240.	239.5	239.5
Vanadium ..	51.0	51.4	51.4	51.2	51.2
Ytterbium ..	171.9	173.2	173.	173.	173.
Yttrium ..	88.3	89.0	89.0	89.	89.
Zinc ..	64.9	65.4	65.40	65.4	65.4
Zirconium ..	89.7	90.4	90.5	90.6	90.6

ON THE ESTIMATION OF THE HALOGEN ELEMENTS IN ORGANIC COMPOUNDS.

By A. VALEUR.

IN the course of a number of combustions of chlorinised organic compounds effected with a calorific bomb, I was much struck by the instantaneousness of the combustion, and I asked myself if, besides calorimetric measurements, it would not be possible to apply this particular method of decomposition to the estimation of chlorine, bromine, and iodine in organic matters. A long time ago M. Berthelot described how it is possible to analyse the products of combustion which are found in the bomb.

Again recently (*Comptes Rendus*, cxxix., 1902), he has shown that the use of this apparatus may be applied not only to exact thermochemical measurements, but also to the quantitative estimation of most of the mineral elements susceptible of entering into the composition of organic molecules.

Being led in the same direction by my thermochemical researches on the chlorinised compounds of quinone and of hydroquinone, I carried out a certain number of experiments which led me to adopt a method which has been found to give excellent results.

The methods most often used in laboratories for the estimation of chlorine, bromine, and iodine in organic substances are the lime method and the one known under the name of Carius.

In far the greater number of cases these two methods give very exact results when certain indispensable precautions are taken. Nevertheless, besides some drawbacks peculiar to each, they have a common fault, which is, that they both require a relatively long time for a single estimation. The decomposition of the organic matter is not, in fact, instantaneous, but progressive; further, it is necessary to concentrate, collect, dry, and weigh the silver salt; this complicates the operation, and prolongs the time, so that for a complete determination, no matter which process is employed, five or six hours is required.

The method I propose to describe enables us, on the contrary, to considerably reduce the time, and to make an estimation of chlorine or bromine in about half an hour, or one of iodine in about an hour. On the other hand, however, we require a special apparatus of a fairly high price, viz., Berthelot's bomb. I shall first take the case of chlorine and bromine, and after that the case of iodine.

Estimation of Chlorine and Bromine.

This is based on the two following principles:—

1. When we burn a chlorinised organic compound in oxygen, under pressure, the chlorine of the substance becomes partially transformed into hydrochloric acid and partly remains in the free state, as show by the work of MM. Berthelot and Matignon.

2. Ammonia in excess reacts on the chlorine, transforming it into chloride of ammonium, according to the equation $8\text{NH}_3 + 3\text{Cl}_2 = \text{N}_2 + 6\text{NH}_4\text{Cl}$.

The hydrochloric acid also unites with the ammonia, giving chloride of ammonium. These principles also apply to bromised compounds.

The method thus consists of burning the chlorised or bromised substance in oxygen under pressure in the presence of a pure concentrated ammoniacal solution.

The combustion is instantaneous, and gives rise to the formation of the following products: Carbonic anhydride, free chlorine, hydrochloric acid, and a very small quantity of nitric acid.

The bomb is shaken up immediately after the combustion; the ammonia absorbs the different products formed, and we finally have a solution which contains, besides an excess of ammonia, some carbonate, a little nitrate of ammonium, and the whole of the chlorine in the state of chloride of ammonium.

It is only necessary to collect this solution, which can

be used with the greatest ease, for the estimation of the halogen element by the volumetric method. For this purpose I have made use of two distinct methods of working which have both given me excellent results.

1. The solution is evaporated to dryness on a water-bath; in this manner we get rid of the ammonia and the carbonate of ammonium, without losing the least trace of chloride of ammonium. In fact, this salt is stable at 100° , and, as is described in text-books on chemical analysis, it is possible to estimate the ammonia contained in an aqueous solution, by adding an excess of hydrochloric acid, evaporating down at 100° , and weighing the chloride of ammonium formed.

The residue, consisting of chloride of ammonium and a trace of nitrate, is titrated by means of a solution of nitrate of silver, using neutral chromate of potassium as an indicator.

2. A still more rapid, though just as accurate, method may also be used; for this purpose the ammoniacal solution is collected and made distinctly acid by cold pure dilute nitric acid. To this is added an excess of titrated nitrate of silver, and the excess of silver is determined by means of a titrated solution of sulphocyanide of ammonium, using iron and ammonium alum as an indicator, according to the beautiful method first described by M. Lextreit, but better known under the name of Charpentier or Vöhlard.

I have used both the above methods indifferently for the estimation of a large number of chlorised or bromised substances. I will now give a few results while laying stress on certain experimental details.

1. *Chloranilic Acid*, $\text{C}_6\text{O}_2\text{Cl}_2(\text{OH})_2$.—The acid was purified by several crystallisations in boiling water, dried at 120° , then made into pastilles so as to be easily burnt in the bomb. This substance burns with difficulty, so it is necessary to have recourse to an auxiliary combustible, viz., naphthalene.

The pastille of chloranilic acid weighing 0.3262 grm. was therefore placed between two pastilles of naphthalene, each weighing about 0.20 grm., and the combustion was effected in the ordinary manner in the bomb, at the bottom of which 25 c.c. of ammonia have been previously placed.

The substance burns instantaneously and the bomb becomes heated; it is cooled in a current of water, and shaken up so that the ammoniacal solution will absorb all the gaseous products which have been formed. This done, the gases are allowed to escape in such a way as to prevent the entanglement and loss of any small drops of liquid; the bomb is then opened, and the ammoniacal solution which it contains is collected, and the interior of the bomb washed with the greatest care. These washwaters are added to the ammoniacal liquid, and the whole placed in a porcelain crucible and evaporated to dryness on a water-bath. The residue after evaporation is taken up with a little distilled water, a few drops of neutral chromate of potassium added, and titrated with nitrate of silver. 31.3 c.c. of silver solution were required, corresponding to 0.00354 grm. of chlorine per c.c.; that is—Found, $\text{Cl} = 33.96$; calculated for $\text{C}_6\text{H}_2\text{O}_4\text{Cl}_2$, $\text{Cl} = 33.97$.

2. *Dibromanthracene*.—Weight of substance used = 0.7656 grm.; $\text{NH}_3 = 30$ c.c. The ammoniacal liquors were divided into two parts; in one the bromine was estimated by the chromate method, and in the other by sulphocyanide:—Found, $\text{Br} = 47.45$ and 47.51 ; calculated for $\text{C}_{14}\text{H}_8\text{Br}_2$, $\text{Br} = 47.72$.

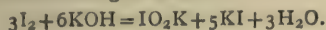
3. *Parabromobenzoic Acid*.—Two experiments were made; one on 0.6573 grm. gave $\text{Br} = 39.44$; the other on 0.5051 grm. gave $\text{Br} = 39.48$; calculated for $\text{C}_7\text{H}_5\text{BrO}_2$, $\text{Br} = 39.80$.

Estimation of Iodine.

Iodised bodies do not behave like the chlorised or bromised compounds when burnt in oxygen under pressure. In fact, the iodine is found after the combustion entirely in the metalloiodic state, or, if a small quantity does pass into the state of hydriodic acid, it will be extremely minute. However that may be, ammonia

cannot be employed in this case, as it can with bromine and chlorine, on account of the different action it has on iodine. I therefore replaced it by an aqueous solution of potash.

The action of potash on iodine is well known; it is expressed in the following manner:—



On the other hand, on adding an acid to the alkaline solution on which the iodine has reacted, this element ought to be set at liberty once more, according to the equation $\text{IO}_2\text{K} + 5\text{KI} + 3\text{H}_2\text{SO}_4 = 3\text{SO}_4\text{K}_2 + 3\text{H}_2\text{O} + 2\text{I}_2$.

Thus, by freely acidulating this solution and distilling, the iodine will pass over with the distillate. Finally, if we add to this acid liquor free from iodine a saturated solution of bichromate of potassium and heat again, the small quantity of hydriodic acid which might have been formed during the combustion will thus give up its iodine.

Such are the principles on which rests the method I propose and which I have just described in some detail.

I have worked on a compound very rich in iodine; viz., tetraiodoethylene, C_2I_4 , utilised in therapeutics under the name of di-iodoform, and in which the estimation of the iodine cannot be effected in the ordinary manner without some difficulty.

This substance was carefully purified by several crystallisations in boiling benzene, and dried away from the light. Its density is too high ($D=4.25$) for so small a quantity as I used to be made into a pastille. This difficulty was got over in the following manner:—

A small cavity was scraped in a pastille of naphthalene, and the iodised compound placed therein, say about 0.2942 grm. in each experiment; above the material was placed a second pastille of naphthalene, and the combustion was made in the ordinary manner in the bomb, at the bottom of which, before the experiment, was placed 50 c.c. of a solution of potash containing two molecules of KOH per litre.

When the combustion is finished the bomb is placed on a flat surface parallel to its greater axis, and rolled about for some time so that the alkaline liquid will be made to touch successively every point of the interior of the apparatus.

When this is done it is allowed to cool, and then only the gases are allowed to escape slowly; they should be perfectly inodorous if the operation has been well carried out. The bomb is then opened and carefully washed. The liquid is placed in a small flask connected with a condenser, the end of which is plunged into an aqueous solution of iodide of potassium.

The alkaline solution is then partially neutralised with sulphuric acid diluted with four volumes of water, and distilled.

When no more iodine passes over and the atmosphere of the flask becomes clear, we add a fresh quantity of sulphuric acid, so as to make the solution strongly acid, then 30 to 50 c.c. of a saturated solution of bichromate of potassium, and distil once more until the last traces of iodine are removed.

Then the iodo-iodised solution is diluted to 200 c.c., and 20 c.c. taken for the estimation of the iodine by means of a dilute solution of hyposulphite of sodium, exactly titrated with pure iodine.

For 0.2942 grm. of material, 21.9 c.c. of hyposulphite were necessary, corresponding to 1.28 grm. of iodine per litre; that is to say—Found, $\text{I}=95.28$; calculated for C_2I_4 , $\text{I}=95.48$.

During the preceding operation it is indispensable to add acid twice, because the alkaline solution is very rich in carbonate, and the addition of too large a quantity of acid would raise the temperature, and might occasion a considerable loss, iodine being carried off by the carbonic anhydride evolved.

The methods described above are equally applicable to the estimation of the halogen elements in liquid and volatile compounds, so long as certain precautions are taken, as described in the "Traite de Calorimétrie

Pratique," by M. Berthelot, and which are but very little trouble.

To sum up, by the complete and instantaneous decomposition of the substance, and by the rapidity and simplicity of the operations, these methods are eminently practicable. Great advantages can be drawn from them especially when a series of estimations has to be made.—*Bull. Soc. Chim.*, Series 3, xxiii., No. 3.

CONTRIBUTIONS TO OUR KNOWLEDGE OF COTTON-SEED OIL.

By B. A. VAN KETTEL.

As far back as 1897 I described a new reaction of cotton-seed oil, a reaction based on the presence, in a certain number of fatty oils, of minimal quantities of pentosanes which are not contained in fats of animal origin. These pentosanes may easily be detected by means of a hydrochloric solution of phloroglucine.

Shortly afterwards, my attention was directed to a very remarkable reaction discovered by Halphen, which is worthy of a few remarks. Equal volumes of the oil under examination, amylic alcohol, and sulphide of carbon containing 1 per cent of sulphur in solution, are placed in a test-tube; this tube is plunged into boiling salt water, and left for ten minutes or a quarter of an hour. At the end of this time the colouration is noticed; if a red or orange colour is produced the presence of cotton-seed oil is indicated.

The numerous coloured reactions proposed for cotton-seed oil are also brought about by certain oils derived from the *crucifera*, so that in such a case the detection of cotton-seed oil is, if not impossible, at least very difficult.

I should like to make a few more remarks on the subject of my reaction.

It succeeds best when we proceed in the following manner: 10 grms. of the oil are poured into a test-tube, treated with a few c.c. of hydrochloric acid ($d=1.06$), and heated for a few moments so that the fumes of the hydrochloric acid come in contact with the whole mass of the oil.

After standing for ten minutes the oil separates completely from the acid layer, a hydrochloric solution of phloroglucine is added, and, after a few minutes, we can distinctly perceive a red ring form on the surface of separation of the two layers. The non-formation of this ring at the end of half-an-hour proves the absence of pentosanes.

Among the oils which give no reaction we may mention the following: Cocoa-nut oil, oil of arachis, sunflower seed oil, and linseed oil.

In my paper "On the Dissemination of the Pentosanes in the Vegetable Kingdom" (*Berichte van der Nederl. Maatschappij ter beoording der Pharmacie*, October, 1897), I did not mention olive oil. This oil, which is of a high price, is very subject to adulteration, and to be able to detect the presence or absence of cotton-seed oil, I thought it essential to first assure myself whether or not it would give the reaction of the pentosanes.

This research is not yet finished, for I have not yet myself been able to prepare any olive oil. Quite recently Professor Welfers Bettink has kindly placed at my disposition a small quantity of olive oil which he himself prepared from the fruit, and, on the other hand, I have received from Spain a sample of oil which has been prepared by a very skilful person worthy of entire confidence.

In neither case have I been able to obtain the pentosane reaction, so that I may reasonably conclude that pure olive oil is free from pentosanes, or, at any rate, that it contains such minute quantities that the reaction is not manifest at the end of half an hour.

In this respect olive oil resembles oil of arachis, and

therefore the detection of this latter becomes difficult. However, in the method of Tortelli and Ruggeri (*Moniteur Scientifique*, 1898, p. 725) we possess a certain test for the detection of oil of arachis in olive oil. I must, however, add that, according to Archbutt (*Journ. Soc. Chim. Ind.*, 1898, p. 1009), oil of ravisson also contains traces of oil of arachis.

In what follows I propose comparing Halphen's reaction with my own, and at the same time I shall describe Carvall's new reaction (*Zeits. für Nahrungsmittel Untersuchung.*, 1898, p. 119). This latter consists of treating cotton-seed oil with a mixture composed of 2 grms. of resorcin, 20 c.c. of water, and 15 c.c. of sulphuric acid; after shaking thoroughly there is produced a red colouration, which quickly changes first to green, and then to blue. It is this blue colour which indicates the presence of cotton-seed oil.

My experiments were carried out on six samples of commercial cotton-seed oil. I first wished to find out whether it was indispensable, for obtaining Halphen's reaction, to heat in a salt-water bath, and I found that to obtain the red colouration it sufficed to heat in an ordinary water-bath for fifteen minutes. Secondly, it appeared of interest to find whether the presence of amylic alcohol is necessary, and I found that this body helps the apparition of the red colour. Finally, I was anxious to make certain whether the addition of sulphur to the sulphide of carbon is absolutely necessary, and I was enabled to observe that, in the absence of this body, the reaction is not so distinct with some oils.

These preliminary researches were fully confirmed later on by Solstein, as well as by Raikow and Tscherenowanow (*Chemiker Zeitung*, 1899, December 6).

Further, these last-mentioned chemists observed that the red colouration took place equally well on exposing the mixture of cotton-seed oil and the reagent to sunlight for a few hours.

In my experiments I left the mixture of oil and Halphen's reagent to boil on the water-bath for twenty minutes.

In Table I. the sign + indicates the apparition of the red colouration, while the sign - shows that it was not visible; the sign $\pm$ indicates that the reaction was hardly perceptible.

TABLE I.

	Halphen.	v. Kettel.	Cavalli.	
Oil A ..	+	+	+	Raw American oil, yellow.
" B ..	+	+	-	Do., free from stearine.
" C ..	-	+	+	Raw Egyptian oil, yellow.
" D ..	+	$\pm$	-	Union.
" E ..	+	+	$\pm$	Miner's white.
" F ..	+	$\pm$	-	Prima summer yellow.
Stearine G	+	+	-	Cotton stearine.

We see that, with sample C, Halphen's reaction is at fault, while my pentosane reaction succeeds very well. It is *a priori* to be expected that Halphen's reaction will not succeed with cotton-seed oils of a deep reddish-brown colour, and, as a matter of fact, I was unable to effect it under such conditions. For this purpose I mixed a certain quantity of raw, brown cotton-seed oil with some animal charcoal, and, after having well shaken, I filtered it. From the clearest portion of the filtrate, still slightly coloured brown, I took 25 c.c., and mixed them with 75 c.c. of oil of arachis, giving, as is known, no reaction by Halphen's method. To a certain quantity of the mixture thus obtained the reagent was added, and then submitted to the action of the boiling water-bath for half an hour. No red colouration could be observed; at the most, all that could be seen was a very faint yellowish-red ring on the surface of the oil; the red colouration, properly speaking, was not manifest either by reflected or transmitted light.

The oils A, B, and D, submitted to similar treatment, gave an intense colouration.

I think it may therefore be concluded that raw brown cotton-seed oil does not contain any body the presence of which can be detected by Halphen's reagent.

As for Cavalli's reaction, I need only say that it has practically no value whatever, as is shown by the results given in Table I.

Table II. is for the purpose of showing the relative values of Halphen's and my own reaction, when it is a question of recognising cotton-seed oil added to another oil. My experiments were carried out on an oil of arachis to which was added 5 and 10 per cent of cotton-seed oil.

TABLE II.

	Halphen, 15 per cent.	Halphen, 15 per cent.	v. Kettel, 10 per cent.	v. Kettel, 5 per cent.
Oil A ..	+	+	+	$\pm$
" B ..	+	+	$\pm$	$\pm$
" C ..	-	-	+	+
" D ..	+	+	+	-
" E ..	+	+	$\pm$	$\pm$
" F ..	+	+	$\pm$	-
Stearine G	+	+	$\pm$	-

It suffices to examine this table to become convinced of the sensitiveness of Halphen's reaction, by which it is even possible to detect the presence of only 1 per cent of oil A.

For detecting cotton-seed oil in butter, I dissolved a certain quantity of butter in benzene, and, after having filtered the liquid thus obtained and driven off the benzene by evaporation, I added Halphen's reagent to the melted fat, and heated for half an hour on a boiling water-bath. In twenty experiments made, I only succeeded in discovering cotton-seed oil in one single case.

These commercial oils are submitted to a series of manipulations for the purpose of improving the smell, taste, and colour, and oils thus treated give negative results with coloured reactions. It is for this reason that oils of bad quality are often submitted to the action of a high temperature.

Holde and Pelgry have observed that certain cotton-seed oils, heated to 220—250° for half an hour, lose their property of producing the red colouration with Halphen's reagent.

To see whether the reaction of the pentosanes also would not be produced under these conditions, I heated the oils on which I was experimenting to 250°, in a paraffin-bath, for thirty to forty minutes. The results obtained are given in the following table:—

	Halphen.	v. Kettel.
Oil A	-	$\pm$
" B	-	$\pm$
" C	-	+
" D	+	$\pm$
" E	-	$\pm$
" F	+	-
" G	-	-

— *Pharmaceutisch Weekblad*, 1899, No. 35.

Cyclopropane Nitrile.—L. Henry.—The body previously designated by the author under the name of ethylenoacetic nitrile, constitutes in reality cyclopropane nitrile. This derivative is obtained by the repeated distillation of γ -chloro-butyric nitrile, over powdered caustic potash. The corresponding acid is, in fact, trimethylene carbonic acid boiling at 181—182°, $D_{25} = 1.551$.—*Revue Trav. Ch. P.-B.*, xviii., p. 228.

LUTEOL, A NEW INDICATOR, COMPARED WITH OTHERS.

By PAUL GLOESS.

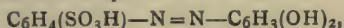
THE different products extolled as indicators in acidimetric and alkalimetric analysis are not really at fault; but, on the other hand, there are but few among their number which are honestly to be recommended.

Let us run through those mostly in use, without, however, criticising them too severely.

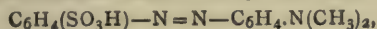
First of all there is tincture of litmus, which is without doubt the indicator most frequently used. Its blue colouration with the caustic alkalis and the alkaline carbonates, and its red colour with the mineral acids, have long been known to all chemists. This indicator would be really perfect if it were not much less sensitive hot than cold, and did it not give intermediate colourations, especially in the presence of carbonic acid. Tincture of cochineal is less to be recommended, seeing that it is not easy for every one to detect the exact point of saturation, the contrast between the red-violet colour with alkalis or alkaline carbonates, and the reddish-yellow colour with acids not being sufficiently pronounced, especially when approaching the point of neutralisation. Further, it is to be remarked that the alkaline solutions of cochineal easily lose their colour on contact with the oxygen of the air, and that the titration must therefore be hurried. These drawbacks appear to have considerably stimulated the search for other more suitable bodies.

New indicators have not been long in appearing since W. v. Miller (*Berichte*, xi., p. 460), and Miller and Kiliani (*Analyt. Chem.*, 1897, p. 71) found that the azoic colouring matters had none of the disadvantages mentioned above.

One of the first products of this class was tropeoline O, or dioxynitrobenzolsulphonic acid—

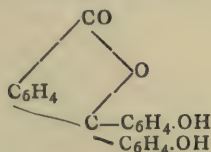


which does not react with carbonic or sulphydric acids. Shortly afterwards M. Lunge (*Berichte*, xi., p. 1940, and Miller and Kiliani, *loc. cit.*) recommended Poirrier orange III., which is also known as helianthine, or dimethylamidonitrobenzolmonosulphonic acid—

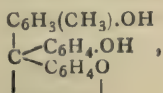


which gives yellow solutions in the presence of alkalis, and rose-red solutions in the presence of acids.

According to Wieland (*Berichte*, xvi., p. 1989, and Miller and Kiliani, *loc. cit.*), ethyl orange appears to have the same properties. Phenolphthalein,—



is used less frequently than these two last. In the presence of alkalis, and of alkaline carbonates, we obtain fuchsine-red solutions, which are decolourised by an excess of acid. This indicator is extremely sensitive, but cannot be used for the titration of ammonia, or for the direct estimation of alkaline carbonates. Rosolic acid,—

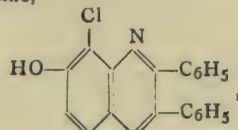


is very restrained in its action. If the contrast in its colouration were more pronounced—acids give yellow solutions and alkalis red ones—it would certainly be much more often employed than it now is. As for the other indicators, we will simply mention the principal ones by name; alizarin, fluorescein, flavescein, nitrophenol,

salicylic acid, hæmatoxyline, Lyons blue, Poirrier's blue, &c.

Like the preceding ones, all these products are more or less subject to different inconveniences; either want of sensitiveness or want of distinct change of colour causing intermediate colouration or a restriction in use, such as, for example, the presence of ammonia, of carbonic acid, &c.

Luteol, which we have used with complete satisfaction in numerous alkali- and acidimetric titrations, does not, however, appear to offer these disadvantages. This new indicator, prepared and recommended by Dr. W. Autenrieth (*Arch. d. Pharm.*, 233, 1), and manufactured by E. Merck at Darmstadt, is nothing else but oxychlorodiphenylchinoxaline,—



It is a derivative of phenacetin, from which it is prepared by the aid of pentachloride of phosphorus, according to the method described in a very interesting paper by Dr. Autenrieth ("Ueber die Einwirkung von Phosphorpentachlorid auf aromatische Aether," *Arch. de Pharm.*, 233, 1). According to this paper phenacetin is successively transformed into nitrophenacetin, nitrophenetidine, *m*-ethoxy-*o*-phenylenediamine, ethoxydiphenylchinoxaline, chlor-ethoxydiphenylchinoxaline, and finally into chloroxydiphenylchinoxaline.

Luteol, crystallised in alcohol, occurs in fine needles with a pale yellow colour, melting at 246°, and subliming at a higher temperature without decomposition. It is insoluble in water, difficultly soluble in cold alcohol, but easily so in warm, as it also is in ether. Completely insoluble in the cold in the mineral acids, luteol is easily dissolved in cold solutions of caustic soda and potash, ammonia, or the alkaline carbonates, giving salts of a very pronounced yellow colouring power. An excess of acid completely decolourises these solutions, precipitating the luteol in the form of a whitish flocculent deposit. The sensitiveness of this indicator is very great. We can still obtain an easily recognised yellow colouration, where phenolphthalein and tincture of litmus no longer react. The change of colouration of solutions from acid to alkaline, or the inverse, is very distinct, and is effected rapidly with a single drop, even when using 1/10th normal solutions.

The indicator is prepared (W. Autenrieth, *loc. cit.*) by dissolving 1 grm. of luteol in 500 c.c. of alcohol. The flasks containing the solutions should be hermetically sealed away from fumes of ammonia gas. As the colouring power is very pronounced, it suffices to use five drops for a titration; further, it is advisable to well dilute the liquid to be titrated.

The advantages possessed by luteol over the other indicators are not without interest. To mention only a few, it can be used for titrations of ammonia (for example, in the important determinations in Kjeldahl's process) and in the hot estimations of the alkaline carbonates. Finally, its great sensitiveness and its sharp change of colour without causing intermediate colourations, often difficult to distinguish, must not be forgotten. The use of this new indicator, therefore, seems to us strongly to be recommended.—*Moniteur Scientifique*, Series 4, vol. xiv., March, 1900.

Oxidation of Trichloro-ethoxy-ethene.—L. Henry. —Trichloro-ethoxy-ethene, $\text{CCl}_2=\text{CCl}(\text{O.C}_2\text{H}_5)$, absorbs dry oxygen, giving a new body which is very similar to the chloride of ethoxydichloro-ethanoyl, $\text{COCl}-\text{CCl}_2(\text{O.C}_2\text{H}_5)$ and which is transformed into oxalic acid by water.—*Rev. Trav. Ch. P.-B.*, xviii., p. 215.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 15th, 1900.

Professor THORPE, F.R.S., President, in the Chair.

(Concluded from p. 153).

*48. "The Sym-dipropyl-, Sym-di-isopropyl-, and aa-Propylisopropyl Succinic Acids." By WILLIAM A. BONE and C. H. G. SPANKLING.

In continuance of their investigations on the alkyl substituted succinic acids, the authors have prepared those which form the subject of the present communication, and show, contrary to the statement of Auwers (*Annalen*, 1898, ccxcii., 164), that each exists in two stereoisomeric inactive forms.

In the case of each acid, each stereoisomeride yields with acetyl chloride its own anhydride (liquid) which with aniline yields a characteristic anilinic acid; each isomeride, on being heated to a high temperature with strong hydrochloric acid under pressure, is to a greater or less extent converted into the opposite form; *trans*-acids are completely converted into *cis*-anhydrides on being heated with acetic anhydride to 170°.

The paper concludes with a discussion of the dissociation constants of the new acids in relationship to those of other alkyl-substituted succinic acids, special attention being drawn to the very great difference between the values for the *trans*- and *cis*-s-diisopropyl acids.

The chief properties of the acids may be thus tabulated:—

	M. p. acid.	M. p. anilinic acid.	Dissocia- tion constant.
<i>Trans</i> .			
s-Dipropylsuccinic	182—3°	184—5°	0·025
s-Diisopropylsuccinic	226	201—2	0·0108
aa-Propylisopropylsuccinic.	192—4	147—9	0·0147
<i>Cis</i> .			
s-Dipropylsuccinic	121°	101—2°	0·049
s-Diisopropylsuccinic	171	184—5	0·2300
aa-Propylisopropylsuccinic.	151—2	Liquid.	0·0295

49. "Manno-galactan and Lævulo-mannan; Two New Polysaccharides." By JULIAN L. BAKER and THOMAS H. POPE.

The authors described two new complex carbohydrates, the one obtained from the Indian clearing nut (*Strychnos potatorum*), and the other from the ivory nut (*Phytolophos macrocarpa*). As these carbohydrates are very stable, the authors have been limited almost entirely to a study of the products obtained by their hydrolysis, these being, for the clearing nut substance, galactose and mannose, and for the ivory nut carbohydrate, mannose and another sugar, which, although not isolated as such, exhibits the characters of lævulose. Having regard to the relative proportions of the different sugars obtained, the authors propose to call the first of these substances manno-galactan, and the other lævulo-mannan. They give no colour reaction with iodine, nor could acetyl- or phenylhydrazine derivatives be obtained.

Manno-galactan.—The powdered clearing nuts are extracted with hot dilute aqueous alkali, and the filtered extract precipitated by means of Fehling's solution; this yields an insoluble, blue, pasty, copper compound, which, after washing, is decomposed with acid, the addition of alcohol to the acid solution then causing the re-precipitation of the carbohydrate. The manno-galactan thus prepared, when dry, is a snow-white, amorphous substance, fairly soluble in cold water and more so in hot; it dissolves readily in dilute caustic alkali solutions. Its composition corresponds with the formula $C_6H_{10}O_5$, and in dilute aqueous solution it has a specific rotation $[\alpha]_D$ at 15° = +74°. After acid hydrolysis $[\alpha]_D$ has a value of about 58·8°, corresponding nearly with the pro-

portion of two parts of galactose to one of mannose. This ratio is supported by the determination of the mucic acid yielded on oxidation with nitric acid. The *dibenzoyl* derivative, $C_6H_5O_2Bz_2$, of the manno-galactan is amorphous and dissolves in benzene, alcohol, and acetic acid, but gives no definite melting-point; in a glacial acetic acid solution, its specific rotation $[\alpha]_D = +23°$.

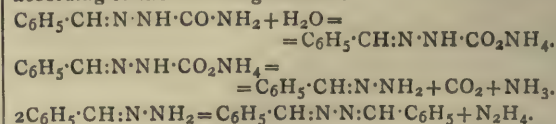
Lævulo-mannan.—As this substance undergoes decomposition in contact with hot aqueous alkali, the extraction of the ivory nut turnings is carried out in the cold, the alkaline liquor being then precipitated by means of Fehling's solution. After separating and washing the copper compound, it is decomposed with hydrochloric acid, and the filtered acid liquid, on standing, deposits a thick, white precipitate, which is soluble in hot water, but, on boiling the solution, the insoluble lævulo-mannan separates out. After drying, the lævulo-mannan is obtained as a white, amorphous substance having the composition $C_6H_{10}O_5$, and its specific rotation in dilute alkali $[\alpha]_D = -44·1°$. After hydrolysis with acid, $[\alpha]_D$ becomes +9·5°; this corresponds nearly with the proportion twenty parts of mannose to 1 of lævulose. Approximate determination of the mannose by the hydrazone method shows that at least 90 per cent of the mixed sugars consists of mannose. The *dibenzoyl* derivative, $C_6H_5O_2Bz_2$, prepared by the Baumann method, is an amorphous substance soluble in benzene, alcohol, and glacial acetic acid, which has in the last-named solvent a specific rotation $[\alpha]_D = -74°$.

50. "Hydrolysis of Semicarbazones." By GEORGE YOUNG, Ph.D., and ERNEST WITHAM, B.A., B.Sc.

The publication by Kipping of a "Note on the Decomposition of Semicarbazones" (*Proc. Chem. Soc.*, 1900, p. 63) necessitates a preliminary notice of an investigation on which the authors are engaged. Some time ago they observed that hydrazodicarbamide gradually disappeared when boiled with water for some days, ammonia and carbon dioxide being evolved. By heating hydrazodicarbamide with water in a sealed tube, they were able to control the hydrolysis, and to obtain a solution the properties of which showed that it contained the first product of hydrolysis, ammonium semicarbazidocarbonylate, $NH_2 \cdot CO \cdot NH \cdot NH \cdot CO_2 \cdot NH_4$. When an aqueous solution of this salt is heated in an open vessel, it rapidly dissociates into ammonia, carbon dioxide, and semicarbazide, the latter being then further hydrolysed.

The authors have studied the hydrolysis of other similarly constituted substances, amongst among them benzalsemicarbazone. When boiled with water in a reflux apparatus, benzalsemicarbazone gradually acquires a yellow colour, due to the formation of benzalazine. Heated with water in a sealed tube, the benzalsemicarbazone dissolves to a colourless solution, which yields benzalazine on boiling, or more quickly on addition of sulphuric acid. In both cases, carbon dioxide is evolved. The filtrate from the benzalazine yields a further quantity of that substance on shaking with benzaldehyde.

The formation of benzalazine from benzalsemicarbazone when the latter is boiled with water takes place apparently according to the following scheme:—



In the formation of the azine from benzylparatolylketone, quoted from Kipping, the process would doubtless be hastened by the presence of free acetic acid.

The investigation is being extended to the corresponding thio-compounds and to substituted hydrazodicarbamides.

51. "The Dissociation Constant of Azoimide." By CHARLES ALFRED WEST, A.R.C.Sc.

The dissociation constant of azoimide in aqueous solution was determined some years ago by Ostwald, but no

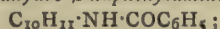
details were ever published. The results obtained by the author agree closely well with those of Ostwald, and show that azoimide as an acid approximates to acetic acid. The values of μ , m , and k are as follows:—

ν .	μ .	m .	k .
10	5.38	0.01397	0.0000198
100	15.98	0.0415	0.0000180
1000	45.97	0.1194	0.0000166

52. "Racemisation occurring during the Formation of Benzylidene, Benzoyl, and Acetyl Derivatives of Dextro-ac-tetrahydro- β -naphthylamine." By WILLIAM JACKSON POPE and ALFRED WILLIAM HARVEY.

On heating dextro-ac-tetrahydro- β naphthylamine carbonate (*Proc.*, 1899, xv., 170) with benzaldehyde on the water-bath, a product is obtained which by fractional crystallisation is resolved into the inactive benzylidene-tetrahydro- β -naphthylamine of Bamberger and Kitschelt (*Ber.*, 1890, xxiii., 876) and benzylidenedextrotetrahydro- β -naphthylamine, $C_{10}H_{11}N:CHPh$; the new substance, which is accompanied by about 20 parts of the isomeride, crystallises in aggregates of colourless needles melting at 58–60°, and, since it is more soluble than the inactive isomeride, the latter is a true racemic compound. The purest sample obtained of the active substance has $[\alpha]_D = +27.6^\circ$ in a 1 per cent solution in alcohol.

Benzoylation occurs readily on treating dextrotetrahydro- β -naphthylamine dextro- α -bromocamphorsulphonate by the Schotten-Baumann method, but the product consists almost wholly of the inactive benzoyltetrahydro- β -naphthylamine of Bamberger and Müller (*Ber.*, 1888, xxi., 850), and contains only a very small proportion of benzoyldextrotetrahydro- β -naphthylamine,—



a larger yield of the latter substance is obtained by adding a solution of benzoic chloride in benzene to a solution of dextrotetrahydro- β -naphthylamine in benzene at 0°. The active benzoyl derivative is isolated by fractional crystallisation from alcohol, being more soluble than its inactive isomeride, and forms less than 5 per cent of the total product. It crystallises in wool-like needles melting at 155–157°, and the highest specific rotation observed was $[\alpha]_D = +58^\circ$ in solution in acetone.

On treating at 0° a solution of dextrotetrahydro- β -naphthylamine in benzene with acetyl chloride dissolved in benzene, a mixture of Bamberger and Müller's inactive tetrahydroacenaphthalide with 2 or 3 per cent of dextrotetrahydroacenaphthalide, $C_{10}H_{11}NH \cdot COCH_3$, is obtained; the active component is the more soluble, and may be isolated by fractional crystallisation from benzene. It forms long colourless needles melting at 104–106°, and the highest specific rotation observed was $[\alpha]_D = 37^\circ$ in a 2 per cent solution in benzene.

During the conversion of dextrotetrahydro- β -naphthylamine into its benzylidene, benzoyl, or acetyl derivative, all but a very small proportion of the primary base undergoes racemisation, and this racemisation apparently occurs prior to the formation of the final product, because the active derivatives are not racemised by heating at 100° either alone or in solution. Racemisation, as a result of operating upon an amido-group contiguous to an asymmetric carbon atom, does not seem to have been observed before, most of the cases, with rare exceptions, such as that of camphor (Kipping and Pope, *Trans.*, 1897, lxi., 956), being of substances in which a hydroxyl-group is attached to the asymmetric carbon atom, and in which the possibility arises of change from an "enolic" to a "ketonic" form. It is important to note that in the present cases the whole of the material is not racemised, indicating that the asymmetric carbon atom in the group $\cdot CH_2 > C \begin{smallmatrix} H \\ \backslash \\ NH_2 \end{smallmatrix}$ never becomes separately bound to only three atomic groups at any stage in the substitution.

Work on these and analogous cases is being continued in the hope of obtaining information respecting the mechanism of substitution in trivalent nitrogen compounds.

NOTICES OF BOOKS.

The Utility of Sulphate of Ammonia in Agriculture. By JAMES MUIR, M.R.A.C., &c.. London: The Sulphate of Ammonia Committee. 1899. Pp. 68.

THE substance of this book is the "Prize Essay on Sulphate of Ammonia," and deals with the whole subject with regard to agriculture.

Sulphate of ammonia, as is well known, is obtained chiefly as a by-product in the manufacture of coal-gas. It is also obtained from coke ovens, blast furnaces, and shale-oil works, and, to a slight extent, in the manufacture of charcoal from bones. The present production in Europe is now estimated at about 400,000 tons per annum.

In agriculture, sulphate of ammonia must be considered as a source of nitrogen only; any other substances which the crops require, and there are ten of them, must be supplied from other sources.

Combined or fixed nitrogen is the only form which can be taken up by plants, and is supplied to them naturally in rain-water, dew, &c., but this to only a very small degree, which has been estimated at 4½ lbs. per acre per annum.

Clover, beans, and other leguminous plants, however, have on their roots small nodules containing bacteria, which have the important power of fixing the free nitrogen of the air, and preparing it for the use of their roots; such crops, in fact, leave the soil in which they grow richer in combined nitrogen, often to a very considerable extent.

The natural supply of nitrogen in the soil is, however, insufficient for the needs of the farmer, and it is obvious that the proper supply in a suitable form must be an essential part of farm management. Numerous experiments on this subject have been made over and over again, both at Rothamsted, Yorkshire, and Norfolk, &c., and many of the results obtained are here given in tabular form in these pages.

Though plants can make use of sulphate of ammonia and other ammonia compounds, yet they are able to use nitric nitrogen more easily. Nitrification, or the process by which organic and ammoniacal nitrogen is changed into the nitric form in the soil, may be described as a series of changes in which nitrogen is made to combine with the oxygen of the air to form nitric acid; this combines with bases forming nitrates. After nitrification the soil is subject to loss of nitrogen by drainage.

The general conclusion arrived at by the author is that, when judiciously used sulphate of ammonia is a most valuable source of nitrogenous manure; but it cannot be used with good effect unless phosphates, and usually potash also, are added to the soil. These mineral manures may be applied to one crop in the rotation and sulphate of ammonia to another, and may be given as artificial or as farm-yard manure; but at some time in a series of years, and in one form or another, minerals must be added, or the use of nitrogenous manures will not prove satisfactory.

Ferric and Heliographic Processes. A Handbook for Photographers, Draughtsmen, and Sun Printers. By GEORGE E. BROWN, F.I.C., late of the G. W. Railway Co. Chemical Staff. London: Dawbarn and Ward, Lim.

To any who use the photographic method for reproduction of drawings, diagrams, &c., this little book will be of value. The subject is dealt with briefly, but thoroughly; minute instructions are given for preparing the various sensitive papers, and every detail of manipulation is explained in a way that shows the author to be thoroughly acquainted with the subject. Those processes that are most generally used are fully described, and a novel feature is to preface the description by giving the *theory in brief*, which greatly helps to form a clear understanding of the process.

At the end of the book is a chapter on the chemicals used, and methods are given for the preparation of some of the more common salts, concluding with an outline of the chemistry involved.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

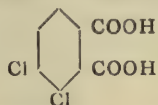
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 11, March 12, 1900.

Action of Hydrogen Peroxide on Barium Oxide.—M. de Forcrand.—The author measured the quantity of heat evolved when H_2O_2 , in varying proportions, acts on BaO ; starting with the proportion $\frac{1}{2}\text{H}_2\text{O}_2$ to BaO and going up to $30\text{H}_2\text{O}_2$ to BaO . From the numbers found, it appears that two successive combinations are formed—one very rich in hydrogen peroxide, and which has never been isolated, the other corresponding to the formula $\text{BaO} \cdot 2\text{H}_2\text{O}_2$. This latter, without doubt, is the well-defined compound isolated by MM. Schœne and Berthelot.

Electrolytic Formation of Potassium Chlorate.—André Brochet.—In a former paper the author describes some results which he obtained by electrolysis of a solution of potassium chloride in presence of chromate. The present paper contains an account of his further researches on the formation of chlorate of potash by simply varying the composition of the electrolyte. He considers the three cases—(a) When the cold solution of potassium chloride is nearly neutral; (b) when the hot solution of potassium chloride is nearly neutral; (c) when the solution is alkaline.

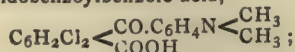
Solubility of Benzophenone.—E. Derrien.—The author measures the solubility of benzophenone in different solvents. All measurements are taken at ordinary temperatures, owing to the recently established fact that benzophenone is easily transformed into an allotropic modification. A list of solubilities is appended.

Dichlorodimethylamidobenzoylbenzoic Acid.—E. Severin.—A. Haller and A. Guyot obtained the dialcylamidobenzoylbenzoic acids by condensing phthalic anhydride with the dialcylanilines in presence of aluminium chloride. An analogous reaction takes place when tetrachlorophthalic anhydride is used, but the tetrachlorodialcylamidobenzoylbenzoic acids behave differently in certain respects from the non-chlor acids. The author starts with Royer's dichlorophthalic acid, 1, 2, 3, 4,—

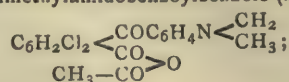


This acid is transformed into the anhydride by simple distillation between temperatures 129° and 140° . From this the following substances can be prepared:—

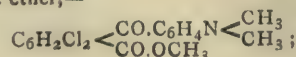
Dimethylamidobenzoylbenzoic acid,—



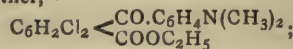
chloracetyl dimethylamidobenzoylbenzoic (a) anhydride,—



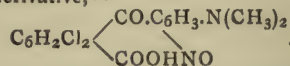
(b) methylic ether,—



(c) ethylic ether,—



(d) nitroso-derivative,—



Acetals of Phenols.—R. Fosse.—As a general rule, the acetals of phenols cannot be prepared in the same way as the acetals of alcohols. When aldehydes react on phenols, whether in presence of acids, or in presence of dehydrating agents, as a rule acetals are not produced, but biphenolic products of condensation, discovered by Baeyer, corresponding to the formula $\text{R}-\text{CH} \begin{array}{l} \text{C}_x\text{H}_y-2-\text{OH} \\ \text{C}_x\text{H}_y-2-\text{OH} \end{array}$. Having easily obtained acetals of β -binaphthol by double decomposition between the aldehydic chlorides and sodic binaphtholate, the author prepares from this substance various unknown acetals.

TO CORRESPONDENTS.

Mechanic.—No such alloy is known.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2107.

ACTINIUM: A NEW RADIO-ACTIVE ELEMENT.

By A. DEBIERNE.

I SHOWED in a previous paper that there exists in residues from pitchblende, apart from the radium and polonium discovered by M. and Mme. Curie, a new radio-active substance belonging to the iron group. I further showed that this substance was precipitated by the principal reagents for titanium.

I have continued my researches with the object of obtaining this body, and I have proved that titanium does not resemble it in all its reactions. In addition to the reactions common to all the elements of the iron group (precipitation by ammonia, ammonium sulphide, soda, sodium carbonate, &c.), the following methods appear to be the best to concentrate the new substance:—

1. *Precipitation of the Boiling Solution, slightly Acidulated with HCl, by excess of Sodium Hyposulphite.*—The radio-active property is found to reside almost entirely in the precipitate.

2. *Action of Hydrofluoric Acid and Potassium Fluoride on the Freshly-precipitated Hydrates suspended in Water.*—The soluble portion is only slightly active. This method is useful for the separation of titanium from the new substance.

3. *Precipitation of the Neutral Nitrate Solutions by H_2O_2 .*—The precipitate contains the radio-active body.

4. *Precipitation of the Insoluble Sulphates.*—Each time that an insoluble sulphate (e.g., barium sulphate) is precipitated in a solution containing this body, the latter is retained, the precipitate being strongly radio-active. This process, which I have found most useful, is entirely different from methods usually employed for the separation of elements.

Oxalic acid, which precipitates the radio-active material well when it is mixed with a tolerably large proportion of the rare earths, seems to be much less efficacious when a number of elements unprecipitated by oxalic acid are present.

These different reactions cannot yet be considered as belonging definitely to the new radio-active substance, because up to the present it has not been obtained sufficiently concentrated. I believe rather that these reactions should be looked upon as the result of retention, analogous to that of iron oxide by barium sulphate.

By using, in a methodical manner, the different methods described above, I was able to extract from the residues of pitchblende the greater part of this new substance which the mineral contained.

The chemical reactions of the most active substance which I obtained, together with the spectroscopic examination, kindly undertaken by M. Demarçay, show that it chiefly consists of thorium. I cannot, however, be sure that it resembles thorium in all its reactions.

If we add a salt of barium or of bismuth to a solution of this substance we can very easily, by the action of ammonia, or H_2S , eliminate the substance having the radio-active property, thereby proving it to be neither radium nor polonium.

I therefore suppose that it is due to the presence of a new radio-active element which I shall call actinium.

It is possible to produce, with the rays emitted by actinium, the same phenomena (fluorescence of barium platinocyanide, photographic impressions, ionisation of

gases) as those of the rays emitted by radium and polonium.

Similarly I was able to repeat with this body the experiments MM. Giesel, Meyer, and V. Schweidler and Becquerel on the action of a magnetic field. Under the influence of an intense magnetic field the rays of actinium, or rather a portion of the rays, are deviated, and will impress a photographic plate situated below a lead cell containing the substance.

The deviation is in the same direction as that of the rays of radium or of cathode rays, i.e., it corresponds to a negative charge of the rays.

Finally, actinium, only very feebly, provokes the induced permanent radio-activity discovered by M. and Mme. Curie on bodies placed in contact or near other radio-active substances. We know that thorium compounds are slightly radio-active. We know further, from what has been said, that actinium seems to be an element allied to thorium. We can therefore suppose that the radio-active property observed in thorium compounds does not belong to this element, but is due to a foreign material. Recent experiments on the radio-activity of thorium made by Rutherford lead also to the same supposition. I propose therefore to try whether it be possible, by utilising the reactions described above, to deprive the thorium compounds of their radio-active property, or to extract from its compounds a substance identical with the actinium extracted from pitchblende.—*Comptes Rendus*, cxxx., No. 14, April 2, 1900.

A NEW METHOD OF SEPARATION OF THE GADOLINITE EARTHS AND PREPARATION OF PURE YTTRIA.*

By W. MUTHMANN and R. BÖHM.

THE neutral chromates of the rare earths are slightly more difficultly soluble than the corresponding sulphates; if a neutral solution of any salt of the cerite or gadolinite earths is treated with potassium chromate solution, precipitates are obtained (even at great dilution), which after washing free from alkali correspond, when crystalline, to the general formula, $R_2(CrO_4)_3 + nH_2O$. The water content varies with the temperature and the nature of the metal; the chromates mostly crystallise with 8 molecules of water. There certainly exist also, as in the case of the sulphates, other hydrates, which have not yet been examined more closely.

These neutral chromates of the earths afford, as we have discovered, an excellent means for separating earth mixtures; we have been able in comparatively little time, by fractional precipitation with potassium chromate, to accomplish separations which were only attained by formerly used methods with great expenditure of time and material. From this follows the remarkable fact, as we shall presently show, that in fractionating the end is attained most quickly by treating the easily soluble dichromates with yellow potassium chromate. Our experiments are applicable both to the cerium and yttrium earths; the work on the latter group shall now be detailed. When an earth mixture is to be fractionated by precipitation which consists, like the commercial so-called yttria material, of six or more components, a number of rules should be applied in the manipulation, which, though they may appear irrelevant, influence in great measure the success of the separation. In our case—we will now describe our most successful fractionation of the dichromate with potassium chromate—numerous test-experiments indicated the following conditions for the quickest possible separation:—

* *Berichte Deutsch. Chem. Gesell.*, Part 33, No. 1.

1. The solution both of the earth salt and of the potassium chromate must be very dilute.

2. The liquid, during the whole precipitation, must be kept boiling rapidly.

3. The resulting precipitate must be finely divided, and brought into the most intimate possible contact with the liquid.

In order to fulfil these conditions we have adopted the following plan in our experiments:—The liquids for precipitation were heated nearly to boiling in large tubular retorts, and then a stream of steam was led in; to avoid spitting, the necks of the retorts were sloped upwards. Besides the steam delivery tube, there was a second tube, fitted with a stop-cock, which allowed the potassium chromate solution to drop in slowly from a calibrated glass flask. This tube was so arranged that the small amount of precipitation caused by each drop was immediately distributed throughout the whole liquid, which was kept in violent motion. In order to work under similar conditions the liquid was always brought to the original volume by evaporation after each fraction. Our first experiments were carried out in such a way that the chromate solution dropped into the boiling liquid, kept in motion by a stirrer; the effect was also tried at each experiment of pouring in all at once the whole of the chromate solution, reckoned for the single fraction, and of finely dividing the precipitate by boiling and stirring; but the result showed that in neither case was the separation so successful as in the method first described. The time saved is lost again afterwards by the necessity of more frequent repetitions of the precipitation.

The dropping is especially necessary, as otherwise the chromates precipitated are mostly amorphous, and are not crystallisable even after several hours' boiling.

We have now applied the above described method to the most heterogeneous earth mixtures, and in this connection will describe a few test experiments, which afforded us a means of obtaining the purest yttria in relatively short time. We started with an earth mixture that is brought into the market under the title "pure yttrium oxide," and in reality only consists partly of yttria, and contains as well oxides of nearly all the remaining rare earths.

We found, with the help of the absorption spectrum, 12–15 per cent erbium oxide; there were also slight indications of the oxides of neodymium and praseodymium; in working with larger quantities we later obtained fractions showing samarium lines. The hydrogen peroxide reaction showed traces of cerium; the cathode luminous spectrum contained the line in the orange characteristic of gadolinium; in short, all the rare earths that could be detected by the help of simple reactions were found to be present in our mixture in greater or less degree.

In order to determine the proportion of this oxide by the above described fractionation method, 40 grms. were pounded with about 90 grms. chromium trioxide, and introduced into 1 litre of water, whereupon, with violent action, solution into the dichromate resulted. The liquid was then treated with potassium chromate solution, till it began to get cloudy, and placed in a 2 litre retort, the whole being so worked so as to give six fractions, which were now examined separately.

Fraction I. a, obtained in two hours with 250 c.c. of 10 per cent potassium chromate solution, yielded only 1.1 gm. oxide, for the earth solution obviously yet contained polychromates. The chromates were quite dark brown, and the oxides much more darkly coloured than the original material. The absorption spectrum showed a distinct increase of erbium oxide; while a 10 per cent solution of the original did not show the red erbium bands, the latter were distinctly visible in the first fraction. The didymium spectrum was also strengthened.

Fraction II. a, obtained like the first, consisted of 34 grms. of light yellow, fine, crystalline needles, with straight extinction. The oxalates were coloured a beautiful deep pink, and gave 13.6 grms. oxide. In this case also

was observed an increase of erbium oxide. The oxides contained about 20 per cent of it. They possessed a much deeper tint, extending more into the orange than the original oxides, which indicates increase in gadolinium.

By evaporation of the solution to the original volume of 1 litre,—

Fraction II. b was obtained, 10.5 grms. chromate, which yielded 6.04 grms. oxide. Crystallisation gave three different bodies:—

1. Fine yellow needles, as with *Fraction II. a*.
2. Orange-red, thick, many sided prisms, almost like potassium bichromate, strongly doubly refractive.
3. Shining crystalline crusts of uniform olive-green colour, apparently consisting of regular octahedra, weakly doubly refractive, which form about two-thirds of the fraction.

As the chromates of *Fraction II. a* yielded about 40 per cent oxides, and those of *Fraction II. b* about 58 per cent, we must conclude that the latter contained less water of crystallisation than the former, which is remarkable, for the temperature of formation of both salts was the same. Still more remarkable was the fact that the oxides of both fractions were scarcely distinguishable in colour and content of erbium.

Fraction III, was obtained with 300 c.c. of 5 per cent potassium chromate solution; 17.6 grms. precipitate, consisting of a quantity of the yellow needles and orange-coloured prisms. From this was obtained 7.04 grms. oxide, of colour almost the same as the original material. Erbium content about 10 per cent; didymium lines scarcely visible. On evaporation of the filtrate only small quantities of the chromate were obtained, which altogether gave 0.4 gm. oxide, and these were added to *III*.

Fraction IV, gave a similar quantity of two different kinds of crystals, treated just as *III*. The two varieties were separated mechanically from each other and carefully examined, with the result:—Orange-coloured prisms, 7.85 grms., yielding 2.55 grms. oxide, = 32.5 per cent; light yellow needles, 7.00 grms., yielding 2.8 grms. oxide, = 40 per cent. The yield of oxide was therefore less in this case than in the previous fractions, which indicates an increase in an earth of small equivalent, viz., yttria. In fact, both fractions exhibited a diminution of erbium; they contained only about 2.5 per cent of it. The oxalates appeared still only in small quantity. The solutions were no longer coloured. Also the content of gadolinium was diminished, to judge by the colour of the oxides. No material difference could be discovered with the spectro-scope between the two oxides. On evaporation of the solution we obtained the dark orange coloured chromate of a still lighter earth; 7.5 grms. gave 2.065 grms. oxide, = 27.4 per cent. The oxide was almost pure white; the erbium spectrum in the solution only indicated.

Fraction V, carried out exactly as in the two former, yielded chromates of almost pure yttria directly, as well as by evaporation of the filtered liquid. These consisted of beautiful orange-coloured prisms; 4.2 grms. oxide were obtained directly, 1.5 grms. by evaporation. Colour of the oxide pure white; no trace of absorption spectrum, even in very concentrated solution.

Fraction VI, gave an oxide in almost exactly the same state, representing the remainder of the earths to be found in the solution, from which arose 1.5 grms. oxide, = 27.4 per cent. The precipitate was obtained from great excess of potassium chromate, 250 c.c. of a 10 per cent solution, in order to throw down all the earths. In this case also the precipitate was uniform, and consisted of deep red-coloured short prisms.

The remaining solution, from which nothing more was precipitated by potassium chromate, was treated with caustic soda; the precipitate contained magnesia, lime, silica, and traces of yttria.

(To be continued.)

NOTE ON THE
ESTIMATION OF MANGANESE IN STEEL.

By HORACE JERVIS.

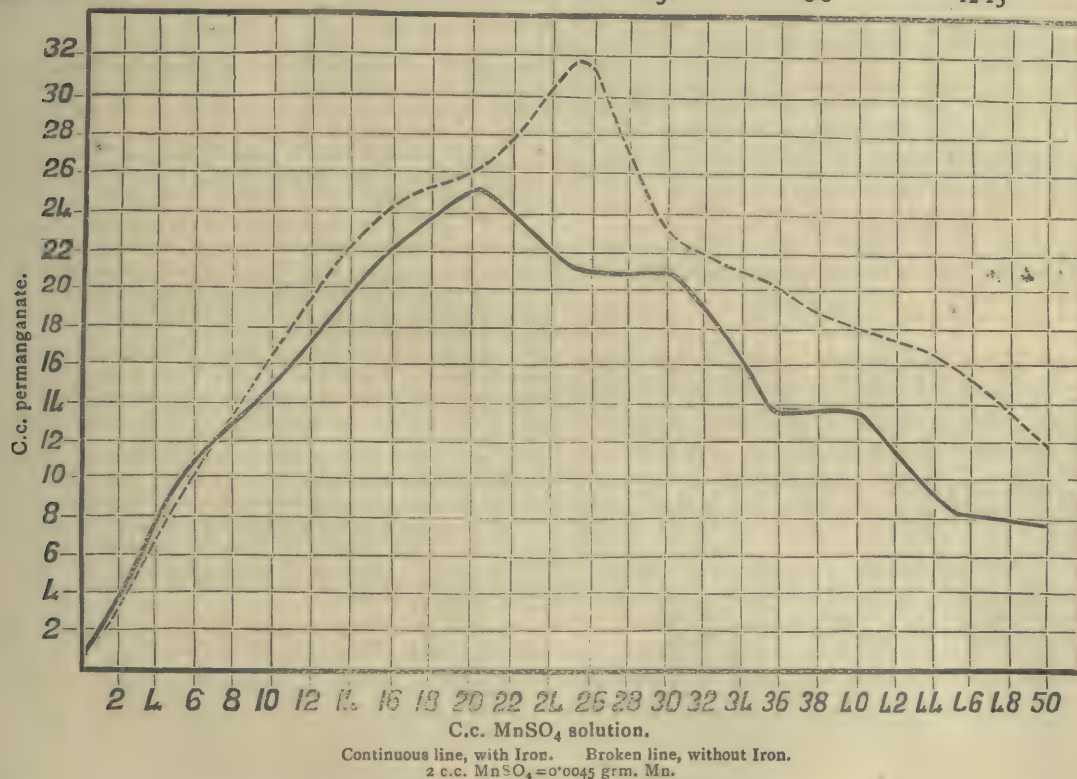
THAT process is referred to whereby the Mn is oxidised to permanganate in an acid solution with Pb_3O_4 or PbO_2 . Perhaps no other process has been so often described under the heading "A New Process for Estimating, &c." It may be a dangerous matter to meddle with questions of priority, but it is certainly somewhat confusing to hear of Deshay's process, Peter's process, Chatard's process, Textor's process, and so on, when one is unaware that essentially one and the same process is meant.

Without doubt the process is a reliable one within very narrow limits, and there does not seem to be much to choose between the well-known modifications of it, except in special cases. I can speak with greatest confidence, however, of that modification in which the sample is dissolved in nitro-sulphuric acid, oxidised with red-lead, and the filtrate titrated with ferrous sulphate and permanganate.

stronger as the manganese increases, and is so unexpected that it seems worth while to illustrate it.

In one series of experiments 1 gram. of bar iron, with increasing amounts of manganese, was oxidised with red-lead in the usual way; another series was treated in the same way, but no iron was present. The amounts of manganous sulphate solution added and the permanganate found in the filtrate expressed in terms of a standard solution are shown in the table and plotted in the curve.

MnSO ₄ solution added. C.c.	C.c. permanganate found.	
	Iron present.	No iron.
2	3'45	3'35
5	9'84	8'5
10	14'8	16'45
15	21'0	23'55
20	24'7	25'85
25	21'15	30'94
30	21'0	22'9
35	14'6	20'94
40	13'75	18'0
45	8'3	16'2
50	8'0	12'15



One per cent of manganese, using 1 gram. of the sample, is properly regarded as the extreme limit within which accurate results are obtainable, but samples up to 2 per cent can be assayed if $\frac{1}{2}$ gram., or up to 4 per cent if 0.25 gram., is weighed off, and so on until a limit is imposed by the delicacy of the operation.

In the ordinary use of the process, the iron is distinctly favourable to the conversion of MnO into permanganate, —more permanganate is obtained with it than without it, —but either with or without iron the recovery of manganese falls appreciably short when somewhat less than 0.09 gram. manganese is present.

This deficiency augments very rapidly until we reach a point beyond which the more manganese one puts in the less one gets out. This conclusion limits Deshay's statement (CHEMICAL NEWS, xxxviii., 70) that the colour is

This peculiarity of the process is more serious than at first sight it appears to be. It means that with perfectly strange material one has to decide whether the percentage recorded is that actually present, or a mere fraction of a much larger percentage. I am aware of an instance in which 0.40 per cent of Mn was returned when really 13 per cent was present, and a 20 per cent spiegel or an 80 per cent ferro-manganese, treated like an ordinary steel, shows not even the slightest trace of manganese. Permanganate is momentarily formed, however, just as the red-lead is added, and may be formed permanently by adding more and more red-lead.

Aluminium has no effect on this process; copper and nickel no further influence than is exercised by their colour in the filtrate. Molybdenum does not interfere. In fact, the process may be used for estimating small amounts of

manganese in commercial metallic molybdenum powders, if the precaution be taken to filter off associated tungsten and graphite. Tungsten steels may be safely assayed for manganese by this process, but grey pig-irons in our experience, even when the graphite has been filtered off, or otherwise destroyed, give somewhat lower results than the gravimetric estimation. Any chromium present is oxidised to chromic acid, and this interferes with the process more or less according to the substance used for titrating the permanganate. Ferrous sulphate cannot be used; it reduces bichromate almost as readily as it does permanganate when the two are present together.

When ammonium oxalate is used for titrating the permanganate the results are very satisfactory. The most convenient and at the same time accurate practice is as follows: Gauge the approximate percentage of manganese in the sample by the colour of the filtrate, run from a burette into the heated (70–80° C.) solution as much ammonium oxalate as will certainly destroy the colour without leaving a great excess, and go back as quickly as possible with standard permanganate. The colour changes from lemon to orange when only a trace of permanganate is in excess. The volume of solution titrated should be about 400 c.c. An excess of oxalate should be avoided as far as possible because it slowly reduces the chromic acid.

The chromic acid may now be titrated with ferrous sulphate for the estimation of the chromium, but the results are considerably low if several per cents chromium happen to be present. If the lead peroxide residue be treated with dilute hydrochloric acid the chlorine expelled by boiling, and that portion of chromic acid added to the results which was present in the residue, the results are sometimes as much as two-tenths per cent low.

A NEW COLOURED REACTION OF TYROSINE.

By G. DENIGÈS.

THERE are, up to the present time, four coloured reactions of tyrosine known; the first is due to Piria, the second to Hofmann, the third to Schérer, and the last to Bertrand. This latter one, of a bio-chemical order, has been specially studied and applied by Bourquelot and his pupils.

Piria's reaction is obtained by dissolving the tyrosine in hot concentrated sulphuric acid; in this manner tyrosine sulphuric acid is formed. This is allowed to cool, is diluted with water, neutralised with carbonate of barium, and filtered. The filtrate, to which ferric chloride is added, gives a beautiful violet colouration. The reaction does not take place in the presence of a mineral acid or on the addition of an excess of ferric chloride.

To obtain Hofmann's reaction we place a small quantity of tyrosine in a test-tube with 2 or 3 c.c. of water and 20 drops of Millon's reagent. This is brought to boiling, and kept at that temperature for a few moments; the solution takes a beautiful red colour, and becomes cloudy owing to the formation of a precipitate of the same colour.

We may also boil the tyrosine with mercuric nitrate, and then add nitrous nitric acid to the liquid.

Schérer's reaction is effected by the careful evaporation to dryness, on a sheet of platinum, of a few drops of nitric acid and tyrosine; in this manner a beautiful yellow residue is obtained, formed of nitrate of nitrotyrosine, which, on the addition of soda, takes a deep orange tint.

It is very evident that these two latter reactions are not practicable in the presence of albumenoid matter, which also causes them, as also do many other substances which behave in the same manner in the presence of Millon's reagent or hot nitric acid.

Piria's reaction, which is not very sensitive, and is difficult to perform, may also be obtained by a number of phenolic bodies, but it cannot be obtained in the presence

of hydrate of carbon and of organic matters in general, which become brown on contact with warm concentrated sulphuric acid.

Of much greater interest is the Bertrand-Bourquelot reaction, which makes use of the property possessed by tyrosinase (a special oxydase contained by a large number of vegetables, especially mushrooms), of giving, with solutions of tyrosine, a red colouration which eventually turns black.

It suffices, in fact, to add 8 or 10 c.c. of the solution in which tyrosine is to be sought for, a few drops of an aqueous extract of *Russula delica*, previously ground with sand, to see the above-mentioned two successive tints rapidly appear.

The drawback to this beautiful reaction is the necessity of having tyrosinase handy, a substance which is not always easily to be obtained.

Finally, it must not be forgotten that Bourquelot has shown a large number of phenols; their ethers, and their corresponding amidised bodies, are also oxidised in the presence of tyrosinase, furnishing various colourations, of which some are often difficult to distinguish from that given by tyrosine under the influence of the same ferment.

The new reaction which we propose, and which we have discovered, is founded on the property possessed by tyrosine of giving with ethanal (ordinary aldehyde), in a strongly acid medium, a product of condensation of a beautiful rose-carmine colour, having a wide absorption band covering the green and nearly the whole of the yellow of the spectrum.

Ordinary aldehyde, which boils at about 21°, not being very convenient to handle, we used it diluted to one-third with alcohol at 90°, according to the formula—

Aldehyde	5 c.c.
Alcohol at 90°	10 „

For the detection of tyrosine we put in a test-tube 2 c.c. of pure sulphuric acid, and 3 to 5 drops of the alcoholic solution of aldehyde, added by means of a pipette. Care must be taken only to add the aldehydic solution drop by drop, every two or three seconds, shaking the liquid thoroughly after the addition of each drop, which must not be allowed to touch the sides of the tube, but must fall directly into the acid. If these several precautions are not taken we should run the risk of causing the formation of a brownish-yellow tint which would interfere with the subsequent observation of the reaction.

As soon as the mixture is made* we add a small quantity of tyrosine, and shake well; almost immediately the mass takes a more or less decided red colour, according to the quantities present and of an intensity proportional, within certain limits, to the quantity of tyrosine present in the sample.

Thus, by dissolving 1 c.grm. of tyrosine in 1 drop of soda lye and 5 c.c. of hot water, 1/20th of a c.c. of this solution containing 1/10th of a m.grm. of tyrosine, gave a beautiful red tint with the aldehydic reagent.

With a solution diluted five times, and a sample corresponding to 1/50th of a m.grm. of tyrosine, the tint was still very decided; it was still appreciable when using a solution of 1/10th the strength of the first, which corresponds to 1/100th of a m.grm. of the product in the sample taken, or 0.2 grm. per litre.

As it is easy to use 1/10th of a c.c. of the tyrosinic solution for each 2 of the sulpho-aldehydic reagent, it will be seen that it is possible to detect tyrosine directly in a solution not containing more than 10 c.grms. per litre.

By making a comparative experiment with a titrated tyrosinic solution, it is possible, by the aid of this reaction, to make a rapid colorimetric estimation of tyrosine, not only in aqueous solution, but also in the liquors of pancreatic digestion; albumenoid matters and peptones (free

* This mixture should not be made until the moment it is wanted, as it changes rapidly. In its preparation we can, if necessary, replace the aldehyde by paraldehyde or metaldehyde.

from tyrosine) do not influence the sulpho-aldehydic reaction.

Finally, we can utilise it for the study of the elimination of urinary tyrosine, by concentrating the urine when this substance is present in smaller quantity than 0.10 or 0.20 grm. per litre.

Although this reagent is influenced by certain phenolic products or their ethers, these compounds have no effect except when present in much greater quantities than in the case of tyrosine, and, further, they do not exist at all in most cases when tyrosine is to be sought for.

Formolised sulphuric acid, prepared by adding 1 c.c. of commercial formol to 50 c.c. of pure sulphuric acid, and which constitutes a very stable reagent, is, contrary to precedent, more sensitive with bodies of the phenolic function than with tyrosine. We hope to use it in the diagnosis of urinary phenols.

When, to 2 c.c. of this reagent, we add a little tyrosine, a colouration of dead leaves is developed, slowly in the cold, but instantaneously at 50–60°, finally taking a reddish tinge.

By adding to the liquid double its volume of glacial acetic acid and boiling, the tint changes to green.—*Bull. des Trav. de la Soc. de Pharm. de Bordeaux*, Feb., 1900.

ON THE CADMIFEROUS-ZINC ORES.

By E. JENSCH.

IN most treatises on metallurgy it is stated that the zinc ores of Silesia contain from 2 to 5 per cent of cadmium, but the author has found that the ore at present taken from these mines only contains from 0.04 to 0.306 per cent, or an average of 0.102 per cent.

The blende from the upper Harz district, also reputed to contain a high proportion of cadmium, does not, however, contain more than 0.01 per cent at the most, and sometimes this element is entirely absent.

In all the Saxony ores, the proportion of cadmium present varies from 0.011 to 0.100 per cent; in those from Styria and Carinthia, from 0.003 to 0.140 per cent.

The highest proportion of cadmium—0.46 per cent—was found in a parcel of 208 tons of black blende from Finland; but the blende from Matlock and Warlockhead, as well as the transparent yellow variety from Cunillas, near Santander, also contains more than 0.40 per cent.

In the Swedish and Norwegian blends the proportion varies from 0.047 to 0.40 per cent. The poorest varieties are those from the north of Norway; they only contain 0.008 to 0.010 per cent of cadmium.

Cadmium is also met with in coal, where it probably exists in combination with pyrites. The highest proportion found was 0.008 per cent in a raw coal; the same coal, washed, contained no more than 0.001 per cent.

A large proportion of the cadmium contained in the zinc ores is lost during calcination. The mean, 0.110 per cent, in the Silesian blends, falls to 0.042 per cent after roasting. The cadmium is partly condensed with the flue dust, which contains from 0.22 to 2.02 per cent.—*Berg- u. Hüttenmännische Zeit.*, 1899, p. 14.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd instant, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The following were elected Members:—Messrs. R. T. Glazebrook, E. J. Humphrey, H. S. Maxim, S. W. A. Noble, W. F. Snell, W. J. Tennant. It was announced that the Actonian Prize of 100 guineas had been awarded to Sir William and Lady Huggins for their work "An Atlas of Representative Stellar Spectra." The special thanks of the Members were returned to Mrs. West and Mrs. F. Colenso for their present of a portrait of their father, the late Sir Edward Frankland, K.C.B., D.C.L., F.R.S., Professor of Chemistry of the Royal Institution from 1863 to 1868.

ON THE MANUFACTURE OF CARBIDE OF CALCIUM.

By G. HANEKROP.

1. The Electric Conductivity of Melted Carbide of Calcium.

As this subject does not appear to have been examined, it seems of interest to record the results I obtained from a number of experiments. The measurements were made in the following manner:—

The block of carbide rested on the lower electrode of the furnace; this latter was connected with a copper wire. Further, at two places in the block, through the solid crust to the part remaining fluid, two rods of iron were inserted to which copper conductors were connected. It was thus possible to measure the fall of potential in the lower layers of the block, through a distance of 8 or 10 c.m., and also that between the iron rods to a variable distance. In Table I. we give a part of the results obtained. The figures relating to the intensity of the current and to the fall of potential were obtained by means of ten readings with variable intensities. For measuring the difference of potential we made use of a very sensitive Weston voltmeter reading to $\frac{1}{100}$ th of a volt. The ammeter used, also by Weston, was graduated up to 1000 ampères; thus measurement could not be made beyond these limits.

It can be seen (column 9) that the resistance of melted carbide of calcium is from 430 to 630 times that of mercury; the conductivity varies from $\frac{1}{430}$ th to $\frac{1}{630}$ th.

These variations should be attributed to the differences of temperature in the interior of the block; we are unable, however, to measure these temperatures.

On comparing the values of columns 3 and 6, we notice that the block is of a higher resistance at its lower part; this is accounted for by the fact that when the block has reached a certain height the base no longer remains liquid, but pasty, thanks to the heat still received by conduction or radiation.

This fall of potential in the base of the block occurs to the same degree both in continuous and intermittent manufacture. It is well known that, by the first method, the carbide is run off at certain intervals of time, and that the production is continued in this manner for several days; while, by the second method, the carbide is left in the furnace by constantly raising the upper electrode, so as to obtain a block of carbide. This block is not removed from the furnace until it has sufficiently cooled and solidified.

Now, as the fall in the lower part is already greater than that in the rest of the block, the economy thus obtained—which was looked upon as the principal advantage the continuous process had over the intermittent one—does not appear to be very great, and should be largely counterbalanced by the loss of heat resulting from each running off of the carbide. Further, in the continuous process, it is always necessary to keep a block of a certain thickness, no matter how little, for the reaction to be regular. There is therefore at the base always a layer of more or less solidified carbide, the electric resistance of which is relatively high.

2. The Use of Wood-charcoal in the Manufacture of the Carbide.

The opinion has often been expressed that wood-charcoal is not suitable for the manufacture of carbide of calcium; and this opinion could even recently be seen in print in the *Zeitschrift f. Calcium Carbide Fabrikation*, ii., 416; and iii., 19. A practical test of sufficiently long duration is enough to refute this quite erroneous opinion. For a year and a half wood-charcoal, and especially that obtained from the distillation of wood at the *Adiengesellschaft für Trebertrocknung*, at Cassel, has been found to make an excellent raw material.

On an average, 780 kilogrms. of this wood-charcoal was

TABLE I.

Measurements between the lower electrode and Rod 2.					Measurements between Rods 2 and 3.				
No	Ampères.	Volts.	Ohms.	Ampères.	Volts.	Ohms.	Distance in decimetres between points 2 and 3.	Section of block in decimetres.	Ohms per 1 decimetre in length and of 1 decimetre section
	1.	2.	3.	4.	5.	6.	7.	8.	9.
1.	890	2'14	0'00240	888	0'78	0'00087	1'40	10'17	0'00632
2.	942	1'82	0'00193	974	0'85	0'00088	1'60	11'34	0'00624
3.	876	2'62	0'00300	860	1'40	0'00262	2'00	7'07	0'00572
4.	808	1'90	0'00235	922	1'98	0'00215	3'50	9'07	0'00557
5.	806	2'04	0'00250	762	1'19	0'00163	4'00	10'74	0'00429

used to obtain 1000 kilogrms. of carbide. The utilisation of the electric energy is very high; we can easily obtain 4 to 4.5 kilogrms. of carbide per 24 h.-p. hours; with careful working we have even obtained 4.5 to 4.7, giving about 300 litres of gas per kilogram. The best results and the best utilisation of electric energy are obtained with wood-charcoal rather than with coke, and depend perhaps on the fact that, at the temperature of the arc, the former is more easily transformed into graphite than the latter. Wood charcoal also reacts more easily than coke.

Carbide prepared with wood-charcoal gives a very pure acetylene. The following figures will serve as terms of comparison. There were found in 1 cubic metre of acetylene—

TABLE II.

Acetylene from carbide prepared from wood-charcoal.			Acetylene from carbide prepared from coke from various sources.		
a.	b.		a.	b.	c.
C.c.	C.c.		C.c.	C.c.	C.c.
PH ₂ .. 243	199		236	380	456
H ₂ S .. 73	Not estimated		505	457	Not estimated

If the carbide prepared from wood-charcoal is decomposed by a sufficient quantity of water, it can be used for lighting purposes without further purification. This carbide is also very suitable for portable lamps to which a system of purification cannot be adapted.

3. Analysis.

The determination of the impurities in acetylene gas by Lunge and Cedercreuz's method is done by means of hypochlorite of soda; but, instead of using a tube with ten bulbs to hold the hypochlorite solution, we used two glass tubes 15 m.m. in diameter and 700 m.m. long, simply curved, and penetrated at each end by a small tube. The funnel tube, with a tap, should be about 30 c.m. long, and the reservoir should have a capacity of about 150 c.c. This volume of water suffices for the decomposition of 50 to 55 grms. of carbide of calcium.

We may combine with the determination of the impurities of the gas that of the return of acetylene from the carbide. For this purpose we insert a chloride of calcium tube. We need then only proceed as with a Bunsen apparatus for the estimation of carbonic acid—an apparatus so well known that it is unnecessary to enter into details. From the loss of weight caused by the disengagement of acetylene we calculate the return in gas. One litre of acetylene weighs 1.161 gm. at 0° and 760 m.m. B.P.

Water is used for the decomposition of the carbide; it is useless to add any salt whatever to diminish the rapidity of the reaction. We can almost entirely prevent the formation of steam by placing the flask used for the analysis in a dish full of cold water. Five or six drops of water a minute are let run over it. As nothing but water is used for the decomposition of the carbide, the residue can be used for future analysis.

We must here mention that the globules of ferro-silicon which are sometimes met with in carbide are easily soluble in a mixture of sulphuric and hydrofluoric acids,

while they are almost completely insoluble in hydrochloric, nitric, and sulphuric acids. Carbide of silicon, which is also found with carbide of calcium, is decomposed by fusion with a mixture of carbonate and peroxide of soda.—*Zeitschrift für Angewandte Chemie*, 1899, p. 592.

A REVISION OF THE ATOMIC WEIGHT OF IRON.*

(PRELIMINARY PAPER).

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

It is rather surprising that the atomic weight of a metal so important as iron should have received so little recent attention as it has. Berzelius† was among the first to determine the quantity under discussion; and in order to accomplish the determination he converted Swedish piano-ware into ferric oxide. For many years his very low results, 54.3, was almost unchallenged, when in 1843 Wackenroder called attention to the fact that in some early analyses of ferric oxide Stromeyer and he had found the substance to contain only 30.1 per cent of oxygen, corresponding to an atomic weight of nearly 56. This led immediately to several investigations by Svanberg and Norlin, Berzelius, and Erdmann and Marchand, whose individual results upon the same ratio varied from 55.81 to 56.23, showing without a doubt that the low value was incorrect, and settling the question with all the accuracy necessary in that day. Rivot in 1850 published two poor analyses which shed no further light upon the subject; and the more recent work of Dumas, who analysed the chlorides of iron in 1859, was no more accurate than his similar work on other metals. Since that time no work on the atomic weight worthy of notice has appeared, so that our present knowledge depends upon data obtained over fifty years ago. In the intervening time Stas has taught the world accuracy in chemical analysis, and countless complications and sources of inaccuracy have been discovered which then were unsuspected. The variations of nearly 0.8 per cent in the best determinations (all depending upon the composition of ferric oxide), point with emphasis toward the necessity of a modern determination. Such questions as the possible presence of gases in the oxide, the possibility of incomplete reduction, and the danger of contamination from the containing vessels, should obviously receive attention.

The balance and weights used in the present study were the same as those used in other recent determinations of atomic weights (*Proc. Amer. Acad.*, 1891, xxvi., 242). It is needless to state that the weights were carefully justified, and that all the usual precautions necessary to procure accuracy in such work were observed. All the weighings were reduced to the vacuum standard, and the

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxv., No. 13.

† The references to all the sources of information are to be found in the critical discussion at the close of this paper.

values of the atomic weights refer to the universally accepted standard $O = 16.000$.

One of the most important steps in such an investigation is clearly the choice of the substance to be analysed, and the choice usually requires a careful preliminary qualitative and quantitative study of many compounds of the element under consideration. This work occupied a number of weeks, and in the course of it we found that the preparation of either ferrous or ferric halides in a pure anhydrous state offered so many difficulties that as yet no satisfactory method for the purpose has been devised. Ferric oxide, on the other hand, can be obtained in a variety of ways, hence the choice of the early experimenters seems to have been a wise one. The first step in a systematic treatment of the subject is obviously a repetition of the discordant work of half a century ago, with especial reference to the possible errors noted above.

Owing to the fact that most oxides formed from nitrates are known to include considerable quantities of oxygen and nitrogen (Richards, *Proc. Amer. Acad.*, 1891, xxvi., 281; Richards and Rogers, *Proc. Amer. Acad.*, xxviii., 200), ignition of ferric nitrate as a means of obtaining ferric oxide was at first rejected, and ferric hydroxide was used instead. Very pure iron ribbon was dissolved in sulphuric acid, and the metal was then deposited electrolytically from an ammonic oxalate solution. After the film had been dissolved in the purest nitric acid, the carbon was removed by filtration, and the iron was precipitated as ferric hydrate by the addition of an excess of ammonia which had been distilled into pure water contained in a platinum dish. The precipitate was washed thoroughly, collected upon a pure washed filter paper, separated from the filter paper while moist, and finally dried in a platinum dish upon the steam bath. The lumps of dried hydrate were crushed in an agate mortar and finally ignited for several hours in a current of pure dry air. During the latter operation the weighed platinum boat with the oxide was contained in a large porcelain tube heated by a Fletcher furnace to about 900° . Constant weight within a few hundredths of a milligram was obtained without difficulty. The weighed oxide was then reduced in a current of electrolytic hydrogen which had been dried by means of fused potassic hydroxide. Ferric oxide is only very slowly reduced at the highest temperature which can be used with glass tubes, so that this reduction also was of necessity carried on in porcelain tubes. Even at about 900° ,* long continued heating was needed to complete the reduction, the total period of ignition amounting sometimes to twenty hours. The progress of the reaction was slightly accelerated by alternate oxidation and reduction.

Two analyses, carried out in the fashion described, are tabulated below. Corrections to a vacuum standard have been applied by adding 0.00009 grm. to every apparent grm. of ferric oxide, and 0.00001 grm. to every apparent grm. of metallic iron, the specific gravities of these two substances being assumed to be 5.2 and 7.9 respectively (Landolt und Börnstein "Tabellen," 1894, cxviii., 133).

SERIES I.

Number of analysis.	Weight of ferric oxide in vacuum.	Weight of iron in vacuum.	Atomic weight of iron.
1	3.17485	2.22096	55.885
2	3.61235	2.52750	55.916
Average.. . . .			55.900

The fact that both of these results are considerably lower than the accepted value of the atomic weight of iron (56.0) seemed to confirm a suspicion which had already arisen that ferric hydrate might not be completely converted into the oxide by ignition at a high temperature. That the oxide upon ignition easily reached constant weight is, however, evidence in the other direction. Since

no direct method of proving the presence or absence of retained water was at hand, it seemed best to make use of another method of preparing ferric oxide. Although, as has been already stated, oxides formed from nitrates occlude nitrogen and oxygen, yet these gases are evolved upon solution of the oxides and can be determined. Ignition of ferric nitrate was therefore chosen as the next method of obtaining ferric oxide.

The material used in the following work was purified with great care. In the first place a solution of a so-called "chemically pure" chloride of iron was treated with an excess of sulphuretted hydrogen and the resulting sulphides and sulphur were removed by filtration. From the filtrate, after oxidation with nitric acid, the iron was precipitated with an excess of ammonia hydrate and the precipitate was thoroughly washed by decantation. In this process traces of a number of metals which might have been present must have been removed. The precipitate was dissolved in sulphuric acid, and by cautious addition of ammonic hydrate basic ferric sulphate was thrown down; a precipitate which is much more easily washed than ferric hydrate, but which was re-dissolved in sulphuric acid with considerable difficulty. In order to reduce to the ferrous state the ferric sulphate thus formed, the solution was next subjected to the action of a galvanic current of several amperes. The solution was contained in a large platinum dish which served as the negative electrode, the positive electrode being a flat spiral of platinum wire. Since the solution was very concentrated and contained a considerable excess of sulphuric acid, the greater part of the ferrous sulphate crystallised out when the solution was allowed to cool. By alternately electrolysis and cooling, almost all of the iron was eventually obtained as ferrous sulphate.

The next process in the purification was to deposit the iron electrolytically from a solution of its oxalate. By means of this separation, the aluminum and manganese could be eliminated, since the first, together with alkaline and other impurities, is not deposited by electrolysis, while the second is deposited upon the anode. The ammonic oxalate needed was prepared with great care. Oxalic acid which had been repeatedly crystallised with hydrochloric acid, and then until free from chlorine, was saturated with pure re-distilled ammonia, and the resulting ammonic oxalate was subjected to several crystallisations. To a hot concentrated solution of this ammonic oxalate, the ferrous sulphate was added as long as no permanent precipitate resulted, and the solution was then electrolysed until the greater part of the iron had been deposited. A slight deposit of hydrated manganese peroxide appeared upon the positive pole, which, however, presented enough surface to prevent the deposit from becoming detached. The film of iron was carefully washed and dissolved in pure dilute nitric acid. When all of the ferrous sulphate had been thus converted into ferric nitrate, the solution of the nitrate was filtered and evaporated, and the salt was three times re-crystallised from a large amount of nitric acid. This acid had been distilled in a platinum still and condenser and collected in a platinum receiver. The mother liquor of the first crystallisation was analysed for impurities as follows: After precipitation of the iron as ferric hydrate by the addition of an excess of pure ammonia and filtration, the filtrate was evaporated to dryness and the residue was ignited. Since only a negligible amount of alkaline solid remained, it can fairly be assumed that the final preparation of ferric nitrate must have been free from such impurity. During the latter part of this purification platinum vessels only were employed, and the water and reagents were the purest obtainable.

The next step, that of converting the nitrate into oxide, was carried out in part by gentle heating in an electric oven at about 150° (Richards, *Amer. Chem. Journ.*, 1899, xxii., 45). The resulting cake of basic nitrate, after removal from the platinum dish in which it was contained during the above operation, was crushed in an agate mortar, and the reaction was completed by ignition in an

* At the temperature to which the porcelain tubes were heated pure silver did not melt, while sodic chloride was easily fused.

open porcelain tube at a temperature of about 900° for several hours. The oxide, which was now contained in a large platinum boat, was carefully weighed and again heated. The loss of weight during this second ignition amounted to one-tenth of a milligram, while a third prolonged heating caused a further loss of three-tenths of a milligram. This difference must have been caused by the escape of included gases, and was so small in comparison with the weight of the oxide (17 grms.), that further heating was deemed unnecessary.

The determination of the gases contained in this oxide proved to be a matter of considerable difficulty. At first the method used was that of dissolving the oxide in a Sprengel vacuum in fused acid potassic sulphate. Owing to the fact that the sulphuric acid, which was evolved from the fused sulphate, attacked both the rubber connections used for joining the apparatus, and also the stick potash used as a drying agent, it was uncertain whether the small quantity of gas which was collected in the air-pump was originally included in the oxide. A more successful method was eventually found by dissolving the oxide in hot hydrochloric acid containing stannous chloride. The operation was carried on in an apparatus for determining the gases evolved during the solution of a substance, which has already been described in papers from this laboratory (*Proc. Amer. Acad.*, xxviii., 200). In two experiments half a gm. of ferric oxide yielded a mere trace of gas. Cupric oxide treated in the same way evolved considerable gas, less, however, than that evolved when the same cupric oxide was dissolved in sulphuric acid. It was shown, however, that the gas which resulted upon solution in hydrochloric acid and stannous chloride consisted wholly of nitrogen, and that the volume of this nitrogen corresponded to the nitrogen in the gases set free by solution of the same oxide in sulphuric acid. Although it was evident that the oxygen was absorbed by the stannous chloride, yet, since in the case of all oxides heretofore examined the included gases consisted chiefly of nitrogen, it is fair to conclude that this was so in the case of ferric oxide. Only a trace even of nitrogen was evolved from the ferric oxide, hence this preparation must have been practically free from included gases.

In order to avoid any error due to hygroscopicity, the oxide used for each analysis was bottled in dry air in the bottling apparatus, which has already been described elsewhere (*Proc. Amer. Acad.*, 1896, xxxii., 59). The platinum boat containing the oxide was heated in the hard glass tube, while the air was exhausted from the apparatus by means of a Sprengel air-pump. Dry air was then admitted, and the boat was pushed into the weighing bottle, which was then stoppered and weighed with the usual precautions. Since in two instances repetition of the bottling failed to change the weight of the oxide, subsequently this precaution was omitted.

The oxide was then reduced in the manner already described, constant weight of the metal being attained much more easily than in the case of oxide prepared from ferric hydrate. Five closely agreeing results were obtained from analyses of material prepared as above.

SERIES II.

Number of analysis.	Weight of ferric oxide in vacuum.	Weight of iron in vacuum.	Atomic weight of iron.
3	3.97557	2.78115	55.883
4	4.89655	3.42558	55.891
5	4.35955	3.04990	55.891
6	7.14115	4.99533	55.870
7	6.42021	4.49130	55.882
Average.. . . .			55.883

In order to determine if the reduction had been complete in the last two analyses of this series, the resulting metal was dissolved in cold dilute sulphuric acid. In each case a few tenths of a milligram of black insoluble matter remained, which contained platinum. This impurity

probably came from the alloying of the boat with the iron during the reduction, and hence introduced no error. A trace of ferric oxide also was found. Even if the platinum had been originally present, the combined weight of the two impurities could not have raised the final result more than 0.01 per cent; hence no correction was applied.

One of us (Baxer, *Amer. Chem. Journ.*, 1899, xxii., 363), has recently shown that iron when ignited at a high temperature, has practically no tendency to occlude hydrogen, so that in the present case this possible source of error is excluded. On comparing these results with the two determinations of the first series, one is forced to conclude that the oxide made from the nitrate has essentially the same composition as the oxide made from the hydroxide. The higher value indicated by Experiment 2 was probably caused by incomplete reduction, and the first experiment agrees with the average of the second series.

It is interesting to review the older determinations (a complete list of which is given at the end of this paper) in the light of the experience gained in these analyses. Evidently the occlusion (or better, inclusion) of gases by the oxide is a less serious cause of error in the case of iron than in most other cases, if the temperature of ignition is reasonably high. This is the chief probable error which would tend to make the results too low. The three most probable errors having the opposite effect are:—First, the possible presence of magnetic oxide in the ferric oxide; second, the possibility of incomplete reduction during the analysis of this substance; and third, the possible presence of alkaline, siliceous, or other non-reducible material. Wackenroder seems to have been the only experimenter who thought seriously of the first two of these errors; and none of the early experimenters paid any attention to the last, for until recently glass was supposed by most chemists to be wholly insoluble. Wackenroder's work was perhaps the most intelligently carried out of all the older determinations, although his individual analyses did not agree among themselves quite so well as some of the others. His greatest omission was the recognised lack of purity in his hydrogen, although he could not observe an error due to this cause. It is interesting to note that the average of his six results gives the value 55.82 for the atomic weight in question, while a corrected average obtained by rejecting the two most discordant values gives the value 55.92. The result of the present work indicates a value midway between the two averages. Wackenroder's valuable work does not enter into Clarke's average for the atomic weight of iron, for Clarke was unable to find the original paper.

In order to prepare pure iron for his later work, Berzelius fused his metal with ferrous oxide, but gave no proof of the effectiveness of his treatment. It is not impossible that traces of the oxide may have been held by the iron, as copper dissolves cuprous oxide. Erdmann and Marchand made the ferric oxide, which they reduced quantitatively, by the ignition of ferrous oxalate—a method which invites the presence of magnetic oxide. Maumené's method was the process of filtration used in common analysis, in which the possible errors in both directions are plentiful.

These detailed criticisms, taken in connection with the general lack of accuracy which is to be observed in the quantitative work of half a century ago, seem to show that there is nothing improbable in the present result, 55.88. Of course the analysis of a single compound is never conclusive, so that this result is announced only as a preliminary one, which we shall hope to support or disprove in the near future.

List of Determinations.

		Fe=
1814	Wollaston, from Thenard's Results (<i>Phil. Trans.</i> , 1814, civ., 21)	55.2
1826	Stromeyer, (<i>Pogg. Ann.</i> , 1826, vi., 471). Reduction $\text{Fe}_2\text{O}_3 : \text{Fe}$	55.5

1826	Berzelius (<i>Pogg. Ann.</i> , 1826, viii., 185).	Fe=
	Oxidation $\text{Fe}_2:\text{Fe}_2\text{O}_3$	54.3
1830	Wackenroder (<i>Archiv Pharm.</i> , 1843, xxxv., 279; 1843, xxxvi., 22). Reduction $\text{Fe}_2\text{O}_3:\text{Fe}_2$	55.9
1844	Svanberg and Norlin (<i>Liebig's Ann. Chem. Pharm.</i> , 1844, l., 432; also <i>Berzelius Jahresbericht</i> , 1845, xxiv., 121; and 1846, xxv., 42).—	
	Oxidation $\text{Fe}_2:\text{Fe}_2\text{O}_3$	55.87
	Reduction $\text{Fe}_2\text{O}_3:\text{Fe}_2$	56.09
1844	Berzelius (the same references). Oxidation $\text{Fe}_2:\text{Fe}_2\text{O}_3$	56.02
1844	Erdmann and Marchand (<i>J. Pr. Chem.</i> , xxxiii., 1; <i>Lieb. Ann.</i> , 1845, lii., 212). Reduction of oxide from oxalate $\text{Fe}_2\text{O}_3:\text{Fe}_2$	56.02
1846	Maumené (<i>Ann. Chim. Phys.</i> , 1850, [3], xxx., 380). Oxidation $\text{Fe}_2:\text{Fe}_2\text{O}_3$	56.00
1850	Rivot (<i>Ann. Chim. Phys.</i> , 1850, [3], xxx., 192). Reduction $\text{Fe}_2\text{O}_2:\text{Fe}$	54.2
1859	Dumas (<i>Ann. Chim. Phys.</i> , 1859 [3], lv., 157; <i>Lieb. Ann.</i> 1860, cxlii., 26). Analysis of chlorides	56.2

The results of Magnus, Döbereiner, Capitaine (1841), and Torrey (1888), alluded to by Clarke, are not worthy of serious consideration. See *Smithson, Misc. Coll.*, "Constants of Nature," 1897, v., 287; also iv., 65 (Becker, 1880).

From some of these values Clarke (1897) computed the value 56.021, while Messrs. Landolt, Ostwald, and Seubert (1898) chose the number 56.0.

DETERMINATION OF CALCIUM AND MAGNESIUM IN ASHES.*

By J. K. HAYWOOD.

THOSE who have had any considerable number of ash samples to analyse according to the method adopted by the Association of Official Agricultural Chemists, cannot help having been struck with the extreme difficulty of determining calcium and magnesium. The whole trouble consists in washing the voluminous precipitate of basic acetate of iron and phosphate of iron, which is not only so bulky as to be troublesome, but also commences to run through the filter soon after washing is begun.

The following work was undertaken with the idea of showing that this washing can be entirely done away with, without seriously affecting the accuracy of the results. To do this, the precipitation of the phosphoric acid and iron from the solution of calcium and magnesium was made in a 500 c.c. flask, the solution then cooled to room temperature, made up to the 500 c.c. mark, and well shaken. 250 c.c. of this solution were then filtered off through a dry filter, keeping the funnel covered to prevent evaporation, evaporated to a small volume, ammonia added to get rid of any small traces of iron that might have dissolved in the liquor (nothing like the large amount that comes through the filter when the precipitate is washed), and the solution again filtered. The manganese is removed with bromine and ammonia, and calcium and magnesium determined in the filtrate. It will be noticed that this method does not correct for the volume occupied by the precipitate of basic acetate of iron and phosphate of iron, and it was to show that this correction is immaterial that the following work was undertaken.

For purposes of analysis three powders were prepared: one containing approximately 10 per cent of lime, 31.5 per cent of magnesia, and 86.5 per cent of sand; two con-

taining 20 per cent lime, 5 per cent of magnesia, and 75 per cent of sand; and three containing 30 per cent of lime, 9 per cent of magnesia, and 61 per cent of sand. Ten grms. of each powder were dissolved in hydrochloric acid and filtered to a volume of 500 c.c., aliquot portions being taken for analysis.

Analyses of the above powders showed the following per cents of calcium and magnesium oxides:—

	I.	II.	III.
Lime	9.81 9.85	19.74 19.66	29.78 29.86
Average.. ..	9.83	19.70	29.82
Magnesia	3.69 3.71	5.28 5.26	8.90 8.90
Average.. ..	3.70	5.27	8.90

Aliquot portions were again taken from the solutions prepared as above, and phosphoric acid was added to each portion, amounting in the case of Solution I. to 5 per cent of the total amount of powder used, in the case of Solution II. to 10 per cent of the total amount of powder used, and in the case of Solution III. to 12 per cent of the total amount of powder used. Enough ferric chloride was added to precipitate all phosphoric acid, and these portions analysed according to my method mentioned above, with the following results:—

	I.	II.	III.
Lime	9.80 9.76	19.72 19.80	29.52 29.54
Average.. ..	9.78	19.76	29.53
Magnesia	3.75 3.82	5.21 Lost	8.95 8.93
Average.. ..	3.79	5.21	8.94

Showing practically the same results as those obtained above when no volume of a precipitate was neglected.

In the case of Solution III., a rather extreme case was next tried by adding enough phosphoric acid to correspond to 20 per cent of the original powder. The results were:—

	III.	
Lime	29.74 29.90	Magnesia 9.19 9.21
Average	29.82	9.20

In my work last year on the official ash sample, which contained 9.83 per cent of phosphoric acid, the calcium and magnesium were determined according to the above method with the following results, in triplicate:—

Lime	11.94 11.94 11.97	Magnesia 5.83 5.75 5.77
Average	11.95	5.78

As against an average of lime 11.62, magnesia 5.74, by the other chemist engaged in the work.

The results obtained, arranged in tabular form, were:—

No. 1.	Lime.	Magnesia.
Before adding phosphorus pentoxide ..	9.83	3.70
After adding 5 per cent phosphorus pentoxide	9.78	3.79
No. 2.		
Before adding phosphorus pentoxide ..	19.70	5.27
After adding 10 per cent phosphorus pentoxide	19.76	5.21

* Contribution from the Division of Chemistry, U.S. Department of Agriculture. From the *Journal of the American Chemical Society*, vol. xxi., No. 6.

	No. 3.	Lime.	Magnesia.
Before adding phosphorus pentoxide ..	29.82	8.90	
After adding 12 per cent phosphorus pentoxide	29.53	8.94	
After adding 20 per cent phosphorus pentoxide	29.82	9.20	
<i>Official Ash.</i>			
Washing precipitate	11.62	5.74	
Not washing precipitate.. . . .	11.95	5.78	

In the case of ashes which contain a larger per cent of phosphoric acid than that included in the limits of this paper, a small correction may be necessary for the volume occupied by the precipitate. On account of lack of time I will reserve the investigation of this subject for a future paper.

THE DETERMINATION OF ANTIMONY IN ORES.*

By THOMAS BROWN, Jun.

THE object of this paper is not to present new methods, but, on the other hand, the application of some very old ones which have been agreed upon by the buyers and sellers for determining antimony in ores, and which after trial have been proved to give more closely agreeing and satisfactory results than those formerly obtained by the many more widely used volumetric and gravimetric methods. In addition such observations and innovations in using these methods will here be mentioned as have been made by the writer in an experience of a year or so in analysing the Mexican ores for the large exporters. Only a limited number of commercial chemists, both on this continent and in Europe, are now engaged in doing this kind of work, because of the past wide variation in results frequently reported on the same sample, caused doubtless by the use of methods not so applicable to this class of ores, which is a matter of much importance considering the large shipments made from Mexico. The following list is of interest in showing the percentages of antimony reported on the same samples of Mexican ores by three prominent English commercial analysts before definite methods had been settled upon, and also the necessity for such a procedure. A, B, and C represent the results of these three chemists, B and C being of London, and D the percentage finally agreed upon in settling.

Sample No.	A.	B.	C.	D.
I.	59.96	52.25	56.1	55.6
II.	55.8	53.62	52.0	52.8
III.	57.27	54.02	54.2	54.1
IV.	58.13	54.5	54.8	54.6
V.	60.78	59.23	63.1	60.0
VI.	57.45	53.7	53.6	53.6
VII.	—	53.5	54.4	53.9
VIII.	59.8	53.2	54.9	53.5
IX.	53.2	52.0	57.8	52.6
X.	—	50.4	51.5	51.9
XI.	—	52.4	53.7	53.0
XII.	—	51.7	53.2	52.4
XIII.	—	46.03	47.7	46.8

These ores are known to the trade as "clean ores," it being of rare occurrence to find impurities in the grades shipped other than silica, iron, and lime, which obviously would not interfere with the schemes of analysis used. The metals of the fifth and sixth groups sometimes found accompanying antimony in ores, such as lead, mercury, copper, tin, and arsenic, when found in quantities larger than traces, should be separated from the antimony when

it is to be determined by the method used for sulphides, and also tin and arsenic when the antimony is to be determined by the oxide method. Shipments of ore from an unknown locality should consequently be put through a series of preliminary tests, and it is always advisable to test every sample for the most common impurities such as lead and arsenic; qualitatively for the purpose of modifying the sulphide method, and quantitatively if found in appreciable quantities, because of having to be taken into consideration in estimating the market value of the ore.

Lead is determined both qualitatively and quantitatively as the orange-yellow chromate (PbCrO_4). For the qualitative test the finely ground ore is boiled with concentrated nitric acid for several minutes, and if a sulphide, until the sulphide of antimony is entirely converted into the insoluble white oxide, then cooled and diluted. Ammonia is added in excess, then acetic acid in excess, and the whole heated for several minutes in order to bring the lead salts thoroughly into solution. The insoluble matter is now filtered off, and the filtrate treated with an excess of potassium bichromate, which precipitates the lead as chromate from this ammonium acetate and acetic acid solution. The lead can also advantageously be determined quantitatively in this form from the sulphide precipitate remaining on the filter after separating the antimony from the metals of the fifth group, as will be explained later in the scheme of analysis.

For arsenic a combination of the Canby and Mohr methods is used. One gm. of the finely powdered ore is mixed in a porcelain crucible with 8 to 10 parts of a mixture of equal parts of sodium carbonate and nitre, gradually brought to fusion over a burner or in a muffle, and kept so for five minutes or more. The fused mass is allowed to cool, disintegrated in hot water, and the insoluble matter filtered off. The filtrate is now acidified with nitric acid, and the carbonic and nitrous acid gases boiled off. An excess of an emulsion of zinc oxide, so apparent in the bottom of the beaker, is added, and should an unusually heavy precipitate of gelatinous silica and alumina be produced, a second filtration is necessary, also an extra addition of zinc oxide to the filtrate before the precipitation of the arsenic. This is precipitated as the reddish brown silver arsenate (Ag_3AsO_4) by the addition of silver nitrate in slight excess accompanied by vigorous stirring.

The precipitate mixed with zinc oxide is filtered, washed with cold water until the washings show no silver reaction, and dissolved off the filter with hot dilute nitric acid, catching the solution and washings in a beaker free from chlorine. When cold, this is titrated for silver with an empirical solution of potassium or ammonium thiocyanate, using 1 c.c. of a saturated solution of ferric sulphate as indicator, and titrating to the same pale amber-yellow colour as was obtained in standardising the solution against pure silver. For the standard silver solution 1 gm. of the pure metal is dissolved in nitric acid, boiled to expel red fumes, and diluted to 100 c.c. For the standard thiocyanate solution 9 and 3/10ths grms. of potassium thiocyanate or 7 and 6/10ths grms. of ammonium thiocyanate are dissolved and diluted to 1 litre; then 1 c.c. = 0.010 gm. silver, and 108 silver = 25 arsenic. This same treatment somewhat modified is used in testing the ore qualitatively for arsenic. After fusion, the addition of acid, boiling, and the addition of zinc oxide in excess, the whole is filtered, and the neutral filtrate tested for arsenic as before.

The antimony ores of Mexico most common to the trade are those of stibnite (Sb_2S_3); cervantite (Sb_2O_4) produced by the oxidation of the former; oxysulphides, mixtures of these two with a preponderance of the former; and senarmontite (Sb_2O_3), which is, however, of much rarer occurrence. The composition of the oxide may be inferred from its behaviour when boiled with concentrated hydrochloric acid, with the subsequent addition near the end of the treatment of a few drops of nitric acid. Cervantite

* From the *Journal of the American Chemical Society*, vol. xxi., No. 9.

treated thus is but sparingly soluble, while senarmonite is almost if not completely so. Stibnite is also completely soluble; if, however, the ore be an oxysulphide, as is frequently the case, insoluble oxide of antimony is found in the siliceous residue which is afterwards determined by fusion.

The following analysis of an ore from the State of Oaxaca illustrates this statement in regard to the solubility of these oxide ores: Moisture, 0.3; silica, 8.5; iron oxide and alumina, 1.6; iron pyrites (FeS_2), 0.9; lime and magnesia, traces; cervantite (Sb_2O_4), 3.8; senarmonite (Sb_2O_3), 84.7; total, 99.8. The results of a complete analysis being calculated to their probable composition, left a difference of 88.7 per cent, to be filled by the 70.8 per cent soluble and the 3 per cent insoluble antimony found, and which were calculated to the composition of senarmonite and cervantite as they were shown to be by their solubility.

Upon the behaviour of these ores when treated with concentrated hydrochloric acid plus a few drops of acid and boiling, is based their division into the following three classes for applying the schemes of analysis:—1. The soluble ores—stibnite (and senarmonite); 2. The practically insoluble ores—cervantite; 3. The partially soluble ores—the oxysulphides, stibnite mixed with cervantite.

(To be continued).

NOTICES OF BOOKS.

Elementary Practical Chemistry. By A. J. COOPER, B.A., B.Sc., F.I.C. With 44 Illustrations. London and New York: Whittaker and Co. 1899. Pp. 86.

THIS text-book is intended principally for the use of Students in Science Classes and Schools of Science, and for those who are engaged during the day time and are attempting to pursue their studies during the evening.

The theoretical bearing of the experiments described is only dealt with in outline, the book being merely a laboratory companion, in which the practical directions are made as explicit as possible.

We must again refer to a fault which is common to many elementary books on chemistry, in which some of the illustrations are trivial, and could well be dispensed with; this book is no exception, and would not lose by many omissions.

The Value of Electrical Treatment. By JULIUS ALTHAUS, M.D., M.R.C.P., Lond., &c. Third Edition. London, New York, and Bombay: Longmans, Green, and Co. 1899. Pp. 165.

THOUGH still viewed with a certain amount of suspicion and mistrust, there is no doubt that the use of electricity for medical purposes is gradually becoming more and more understood, and is now a recognised branch of study and teaching in most hospitals, while in the United States and Germany we read "almost every practitioner makes daily use of both the constant and intermittent current in his treatment of disease." The author, having been in intimate touch with this subject during a long professional career, has once more put forward his views on the uses and limits of usefulness of electricity in medicine.

There are two principal forms of electric energy at present utilised in medicine:—

- I. Frictional, or static, electricity.
- II. Current electricity.

This latter kind comprehends no less than six different varieties, such as Galvanism, the constant current from the main; Faradism; D'Arsonval's sinusoidal current; D'Arsonval's current of high frequency and potential, by

which the patient may be traversed by a current of 3000 milliampères at the rate of 500,000 to 1,000,000 oscillations per second; and Morton's static induced current.

After fully describing the apparatus necessary, the author considers the physiological effect of the different kinds of current, both locally and on the brain and nervous system in general.

He then describes the separate electrical treatment of a large number of definite diseases, giving full instructions as to the kind and amount of treatment required.

Though the author must be regarded as something of an optimist, we recommend a perusal of his work not only to the younger medical men who will be most likely to take advantage of its teachings, but also to those to whom it comes more or less as a revelation of ideas smacking somewhat of quackery.

Sugars and their Principal Derivatives. ("Les Sucres et leurs Principaux Dérivés"). By Prof. L. MAQUENNE. Paris: G. Carré et C. Naud. 1900. Pp. 1032.

THE history of sugars forms at the present time a whole chapter in chemistry, which is no less important from the theoretical than from the descriptive or practical point of view; it is, in fact, on the researches of M. E. Fischer that the speculations of isometry in space have found their most solid basis, and the doctrine of asymmetric carbon its strongest confirmation.

Unfortunately the superabundance of facts, with all their accompanying developments, has prevented them being properly studied in any general treatise on chemistry. On the other hand, the work done on sugars is so widely spread over so many pamphlets and journals, that the bibliography of the subject has become very complex. The author has, for these reasons, endeavoured to unite in a systematic manner all the knowledge we now possess on this subject, which has so long occupied his attention.

The result of his labours, which we have now before us, gives eloquent testimony to the careful and systematic manner in which he has accomplished his object.

The volume is well printed and bound, besides being provided with a large index, and will make a handsome and useful book of reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 12, March 19, 1900.

Hydrates of Barium Peroxide.—M. de Forcrand.—Several hydrates of barium peroxide are known, among which the most important are $\text{BaO}_2 \cdot \text{H}_2\text{O}$, $\text{BaO}_2 \cdot 10\text{H}_2\text{O}$, $\text{BaO}_3\text{H}_2\text{O}$, $\text{BaO}_2\text{H}_2\text{O}_2$. The author continues the work announced in a previous paper on the examination of these compounds, preparing them by the addition of dilute hydrogen peroxide to the dissolved baryta in varying proportions. In each case he measures the heat evolved. When a large excess of hydrogen peroxide is used, compounds are formed which are further oxidised than the trioxide, but they are more and more unstable; they are, besides, very highly hydrated, the number of molecules of water having scarcely diminished, even in the last case.

Separation of the Rare Earths.—R. Chavastelon.—M. Urbain has recently shown, in a paper on the separation of the rare earths, how easily thorium and cerium can be separated from lanthanum and didymium. He shows that, in a mixture of these four substances, first thoria is eliminated, and then cerium. The author has been able to obtain satisfactory results by an inverse method—keeping thoria alone, or thoria and ceria, in solution,

whilst producing with the other rare metals compounds insoluble under the conditions of the experiment. Into an excess of hot or cold saturated solution of neutral sodium sulphite the neutral solution of the mixed earths is poured; cerium, lanthanum, and didymium are precipitated in the form of sulphites insoluble in excess of alkaline sulphite, practically the whole of the thoria remaining in solution. The insoluble sulphites are transformed into chlorides by the addition of HCl. The hydrates are precipitated by ammonia, well washed, and then brought in contact with excess of alkaline bicarbonate, the whole being stirred by a current of carbon dioxide; cerium peroxide alone dissolves. The author also describes another method of separation which is not quite so successful.

Chemical Reactions produced in a Solution: Vapour-tension of Solvent.—A. Ponsot.—The author finds that spontaneous and limited reactions, effected at constant temperature and pressure, between dissolved or mixed bodies, modify a homogeneous or heterogeneous system (1) by increasing, up to a maximum value, the vapour-tension of the solvent when it takes no part in the reaction; (2) by increasing, up to a maximum value, the vapour-tension of one of the reacting bodies when this body is produced in the reaction and inversely.

Estimation of, and Variation in, the amount of Cystine contained in Contaminated Waters.—H. Causse.—This paper is unsuitable for abstraction.

MISCELLANEOUS

Glasgow International Exhibition, 1901.—It is officially notified that all applications for space at the Glasgow International Exhibition, which is to be opened in May, 1901, must be lodged not later than the 1st of June with the General Manager, Mr. H. A. Hedley. There are in all eight classes, embracing agriculture, mining, industrial design and manufactures, machinery and labour-saving appliances in motion, locomotion and transport, marine engineering and ship-building, lighting and heating, science, education, music, sports and sporting appliances. Separate sections will be devoted to women's exhibits, archæology, and fine art.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, after Easter:—Dr. Hugh Robert Mill, three lectures on "Studies in British Geography"; Dr. Alexander Hill, two lectures on "Brain Tissue considered as the Apparatus of Thought"; Mr. R. Warwick Bond, two lectures on (1) "Ruskin, Man and Prophet," (2) "Ruskin, the Servant of Art"; Professor Dewar, four lectures on "A Century of Chemistry in the Royal Institution"; The Rev. Canon Ainger, three lectures on "Chaucer"; Professor Stanley Lane-Poole, two lectures on "Egypt in the Middle Ages"; Dr. Alfred Hillier, two lectures on "South Africa, Past and Future"; Sir Frederick Bridge, three lectures on "The Growth of Chamber Music from Allegri's Symphonia (1580—1652) to Haydn's First Quartet" (with musical illustrations). The Friday Evening Meetings will be resumed on April 27th, when a Discourse will be given by The Right Hon. Lord Kelvin on "Nineteenth Century Clouds over the Dynamical Theory of Heat and Light"; succeeding Discourses will probably be given by Professor T. E. Thorpe, Mr. Sydney Lee, Professor J. A. Ewing, Mr. Francis Fox, Sir Henry Roscoe, and other gentlemen.

The Chemical Laboratory at Wiesbaden.—During the Winter Term of 1899-1900 the Chemical Laboratory Fresenius was attended by fifty-seven students. Of these forty-one were from Germany, five from England, two from Luxembourg, and one from Austria, France, Belgium, Italy, Spain, Russia, Sweden, Norway, and the United States of America. There were three assistants in the Instruction Laboratory, and twenty-four in the Versuchsstationen (private laboratories). In the teaching staff of the institution there has been no change. To this body

belong the Directors, Professor Dr. H. Fresenius, Professor Dr. W. Fresenius, Professor Dr. E. Hintz, and also Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and Architect J. Huber. The Summer Term begins on April 24th. In the Winter Term, 1899-1900, besides scientific work, there were many examinations carried on in the different departments of the private laboratory (Versuchsstationen) in the interest of trade, industry, mining, agriculture, hygiene, justice, and government.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Microscopical, 8. Demonstration on the Structure of some Palæozoic Plants, with Sections of the Plants thrown on the Screen, by Wm. Carruthers, F.R.S., President.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

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NOTICE IS HEREBY GIVEN THAT EXAMINATIONS for the ASSOCIATESHIP (A.I.C.) and FELLOWSHIP (F.I.C.) will be held at the LABORATORIES of the INSTITUTE OF CHEMISTRY, 30, Bloomsbury Square, London, W.C., on TUESDAY, July 10, 1900, and three following days. The arrangements for the Examinations depend upon the number of Candidates. Candidates for the Final Examination may be required to present themselves from Tuesday, July 17, to Friday, July 20. Notice will be given to all Candidates whose applications for examination are received and accepted by the Council not later than Thursday, June 7, 1900, on which day the Examination Lists will be closed.

By Order of the Council,

RICHARD B. PILCHER,

30, Bloomsbury Square, London, W.C. Registrar.

"The Regulations for Admission to Membership and Register of Fellows, Associates, and Students of the Institute of Chemistry" may be obtained from Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C., price 1s.

CHEMICAL LABORATORY, WIESBADEN, GERMANY.

(Academical Institution of Instruction, supported by the State, with the right of developing Provision and Food Analysts for the final examination).

Directors. { Prof. H. FRESenius, Ph.D.
Prof. W. FRESenius, Ph.D.
Prof. E. HINTZ, Ph.D.

Practical Instruction in the Laboratory { Prof. H. FRESenius, Ph.D.
Prof. W. FRESenius, Ph.D.
Prof. E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESenius, Ph.D.
Experimental Physics	Prof. W. FRESenius, Ph.D.
Stoichiometry	Prof. W. FRESenius, Ph.D.
Organic Chemistry	L. GRÜNHUT, Ph.D.
Chemical Technology	W. LENZ, Ph.D.
Microscopy, with exercises in Microscopic work	Prof. H. FRESenius, Ph.D. Prof. W. FRESenius, Ph.D. and Prof. E. HINTZ, Ph.D.
Chemistry and Analysis of Foods	Dr. med. G. FRANK.
Hygiene	J. HUBER.
Practical exercises in Bacteriology	
Technical Drawing, with exercises	

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL's Verlag, at Wiesbaden, or to one of the Directors.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2108

A NEW METHOD OF SEPARATION OF THE GADOLINITE EARTHS AND PREPARATION OF PURE YTTRIA.*

By W. MUTHMANN and R. BÖHM.

(Concluded from p. 170).

Atomic Weight Determinations.

FOR the identification of Fractions V. and VI., which, by all their properties, must have consisted of pure yttria, equivalent weight determinations were carried out, the result of which we will briefly state. The final purification was carried out thus:—The oxides were heated for an hour over the blowpipe flame, then dissolved in the purest re-distilled nitric acid, and precipitated with oxalic acid; this operation was repeated four times in platinum vessels. Finally, the nitric acid solution was evaporated in a platinum crucible with pure sulphuric acid twice re-distilled from a platinum retort, and the excess of sulphuric acid removed by gentle heating on a sand-bath. The conversion of the sulphate into oxide is a slow process in the case of yttria; we had to heat for fifteen to twenty hours in the fiercest blowpipe flame before the weight became constant. The results were as follows:—

	Grms.	Fraction V.	Grms.
Sulphate..	1.75582	reduced to vacuum weights=	1.75636
Oxide ..	0.85570	" "	0.85578

$$\text{SO}_3 = 0.90058$$

Hence atomic weight = 90.12 (O = 16).

Fraction VI.

Sulphate ..	2.46505	grms. reduced =	2.46585	grms.
Oxide ..	1.19511	" "	1.19523	" "

$$\text{SO}_3 = 1.27062$$

Hence atomic weight = 88.97 (O = 16).

Cleve found for his yttria, most carefully purified by fractional precipitation of the oxalates, the atomic weight 89.02, which agrees so well with the number found by us for the sixth fraction that we do not hesitate to consider our preparation as absolutely pure yttria, while Fraction V. still contained small quantities of other earths with higher atomic weights.

Specific Weights.

The densities of the oxides afford an excellent means of tracing the advance of a fractionation in the case of the rare earths; and, in the yttria group, which contains earths of widely differing equivalent weights and widely differing specific weights, these important constants often make it possible to dispense with the lengthy equivalent weight determinations. When one considers that the density of yttria approximates to 5, that of erbium to 8.8, and that of ytterbium to 9.2, and that with careful work the pycnometrical method obscures complete accuracy of the determination in the second place of decimals, one sees at once that, with a mixture of two such earths, a density determination approximates to a quantitative method, but in both cases reliable conclusions are inferred as to the

nature of the bodies under examination. We have therefore never omitted to determine these important constants in our work, and give in the following tables the numbers for the above-described fractions; in the last column the volumes of the oxides received from each fraction are added, whose sum obviously must be equal to the volume of the original material:—

Fraction.	Weight. Grms.	Density.	Volume. C.c.
I.	1.1		
II.	19.6	6.06	3.41
III.	7.4	5.62	1.31
IV.	7.3	5.43	1.34
V.	5.7	4.87	1.28
VI.	1.5	4.83	
Original material	41.29	5.62	7.34
			7.35

The correspondence is satisfactory, especially as the weights of the individual fractions were only determined approximately.

As is seen, the densities diminish rapidly from fraction to fraction, hence the earths with greatest equivalent weight are precipitated first.

Fraction III. shows the same specific gravity as the original material. It is remarkable that we found low numbers for pure yttria, viz., 4.83, while Cleve and Höglund give 5.028, and Nilson and Pettersson 5.046. On the other hand, a value 4.842, found by Ekeberg, agrees well with our numbers. The determination will be repeated later with more material.

Another very important fact results from our density determinations, viz., the presence of a considerable amount of an earth in the original mixture, whose specific gravity apparently lies between those of yttria and erbium. If it were assumed that it is principally these two oxides only that are present, the percentage for Yt_2O_3 would be 68.2, and for Er_2O_3 31.8, according to the simple equations—

$$\begin{aligned} x + y &= 100 \\ \frac{x}{4.831} + \frac{y}{8.640} &= \frac{100}{5.620}; \end{aligned}$$

where x and y are the required percentages.

But such a high percentage of erbium is not possible, for the spectroscopic shows a maximum of 15 per cent, and the presence of another colourless earth is necessarily proved. Now it is to be remembered that we noticed three kinds of crystals, viz., red prisms, olive-coloured octahedra, and fine yellow needles. The first are identified as salts of yttrium, for pure yttria solutions yield only such prisms. We consider the octahedra to be rich in erbium, for they occur principally in the first fractions, which show an intense erbium spectrum, and hence the third oxide must be concentrated in the yellow needles. An experiment carried out with more material—about 2 kilogrms.—which one of us has started in conjunction with Postius, will settle this point. We might mention that lanthanum is quite excluded, as it gives with potassium chromate a quite characteristic, apparently amorphous precipitate, which in reality consists of fine crystalline globules. Also the remaining cerite earths, such as thorium, samarium, and gadolinium, do not come into consideration, so that only terbium and ytterbium remain. It is certain that the quantity of yttria in the gadolinite oxide mixtures is less than has hitherto been assumed.

In conclusion, we should like to indicate how unusually quickly the methods we have discovered can be carried out for fractionating earth mixtures. We succeeded in less than a week to obtain from the already described material about 15 per cent yttria in the absolutely pure state. This must be looked upon as a very fair result, for the earlier used methods are very tedious, and for this reason

Cleve is the only one who has hitherto succeeded in obtaining pure yttria; Bahr and Bunsen only arrived at getting an earth of atomic weight 92.63. The remaining rare earths, especially those of the cerite group, can be relatively easily separated by our methods; we shall in a short time publish our results for this group. We may already remark that we have easily succeeded in separating samarium from the monazite oxides.

It naturally requires more exhaustive and laborious experimenting to discover the most favourable conditions for a separation. The idea of precipitating the rare earths fractionally as chromates is not really new, as Krüss and Loose have already studied the influence of potassium chromate on solutions of the nitrates. But they came to no real conclusion, and a repetition of their attempts only showed that it was not a possible means, for, instead of pure chromates, mixtures of these with basic nitrates were produced in amorphous form, and therefore the experience of Krüss and Loose affords no more than fractional precipitation with ammonia.

Inorganic Chemical Laboratory
of the Technical High School, Munich.

ELECTROLYTIC METHOD FOR THE PREPARATION OF ALKALINE CHLORATES, BROMATES, AND IODATES.

By M. MULLER.

FÖRSTER and Jorre (*Fourn. f. Prakt. Chem.*, 1899, lix., p. 53) have recently shown that the electrolytic formation of alkaline chlorates is due to the oxidation of the hypochlorite from the chloride by free hypochlorous acid. Having obtained this result, the question of the influence of other oxidising agents naturally comes forward.

The following table shows with what rapidity equal quantities of acetic, sulphuric, and chromic acids added to a solution of hypochlorite transforms this salt into chlorate.

In this experiment, as in the following ones, the hypochlorite was estimated by Penot's method, the total oxygen by iodometry, and the oxygen in the state of chlorate by difference, following the directions given by Förster and Jorre.

During the action of acids on hypochlorite of potash, the chlorate commences to crystallise after about one hour. A special sample must be taken for the estimation of the total oxygen.

One c.c. of acid is allowed to react on 1 c.c. of the hypochlorite solution, and after seventeen hours the total oxygen in the mixture is estimated. In the case of chromic acid, the oxygen corresponding to the chromic acid is subtracted from the total oxygen, for this acid would also take part in the reaction during the iodometric estimation, as we must admit that its quantity has not varied.

EXPERIMENT I.

10 c.c. of hypochlorite solution were added to—

Time lapsed since mixing.	10 c.c. of hypochlorite solution were added to—			
	10 c.c. water.	13 c.c. normal acetic acid.	10 c.c. normal sul- phuric acid.	10 c.c. normal chromic acid.
	Grms. of oxygen as hypochlorite in 100 c.c.			
10 minutes ..	1.45	0.96	0.92	0.88
35 " ..	—	0.62	0.62	0.42
60 " ..	—	0.55	0.56	0.32
2 hours..	1.45	0.49	0.55	0.26
4 " ..	—	0.41	0.49	0.16
17 " ..	1.44	0.30	0.29	0.10
Total grms. of oxygen in 100 c.c.				
At commence- ment ..	1.52	—	—	—
After 17 hours.	1.52	1.48	1.46	1.49

Since the transformation of hypochlorite into chlorate is greatly accelerated in the presence of chromic acid, one might suppose that by adding chromate of potassium to a solution of chloride of potassium and electrolysis without a diaphragm, the hypochlorite produced would be oxidised into chlorate more rapidly, and that the losses due to the reduction caused by the current would be thus diminished.

To examine the influence of the chromate, two experiments were made according to the instructions given by Cettel (*Zeit. f. Elekt.*, 1895, Nos. 11 and 15).

A glass vessel was used, of 550 c.c. capacity. A strip of platinum of about 29 square c.m. served as the cathode, on each side of which, at a distance of about 1.5 c.m., was a much smaller anode, also of platinum. The electrodes, and a glass tube for the escape of gas, were fixed through the cork which hermetically sealed the vessel. A gas voltameter, a copper voltameter, an ampère-meter, and a voltmeter were placed in the circuit. During the electrolysis several samples of gas were taken. The results are given in the following table. The strength of the current was 4.5 ampères.

EXPERIMENT II.—The Solution contained 30 per Cent of NaCl.

Temperature, 45—50°.

Tension, 3.9 to 4 volts.

$D_c = 0.18$ amp./sq. c.m.

$D_a = 0.075$ amp./sq. c.m.

Time. Hours.	Return from current. Per cent.	Reduction. Per cent.	Decomposition of water. Per cent.
1	52.3	41.3	6.4
2	35.5	53.3	11.2
3	33.4	54.7	11.9
4	33.1	54.5	12.4
18	30.8	56.7	12.5
21	32.8	54.8	12.4

There were 112 grms. of copper precipitated in the voltameter, corresponding to 28.2 grms. of O_2 . The solution contained 9.26 grms. of active oxygen, or 32.1 per cent of the theoretical return.

EXPERIMENT III.—The Solution contained 30 per Cent of NaCl and 0.18 per Cent of K_2CrO_4 .

Temperature, 42—50°.

Tension, 4.1 to 4.7 volts.

$D_c = 0.18$ amp./sq. c.m.

$D_a = 0.075$ amp./sq. c.m.

Time. Hours.	Return from current. Per cent.	Reduction. Per cent.	Decomposition of water. Per cent.
1	83.5	3.8	12.7
2	77.6	2.4	20.0
3	69.5	0.8	29.7
4	71.6	2.1	26.3
18	68.7	2.8	28.5
21	67.9	3.6	28.5

There were 102.05 grms. of copper deposited in the voltameter, corresponding to 25.75 grms. of oxygen. The solution contained 17.92 grms. of active oxygen, or 69.6 per cent of the theoretical return.

An experiment made under the same conditions as the last, but at 10° for twenty-three hours, gave a still better return; perchlorate was also formed in a noticeable quantity. This might be used as a method for preparing perchlorates directly from chlorides.

The return of 69.6 per cent obtained in Experiment III. surpasses, not only anything that was done in neutral solution, but even the best results obtained by Cettel in alkaline solution.*

It can be seen that this result is obtained from the fact that the reduction is greatly diminished; it therefore seems, at first sight, to agree with the suggestion we have already made. The estimation of the quantity of hypo-

* This return is not the highest possible. The author will shortly describe a process by means of which 88 per cent of the theoretical return can be obtained.

chlorite in solution will, however, show that in this case it is not right to form a conclusion with regard to the proportion of this salt from the reduction figures obtained by the analysis of the gases.

The amount of hypochlorite in 500 c.c. of solution was, at the end of Experiment II., 1.15 grms.; at the end of Experiment III., 1.79 grms.; and the last reduction figures obtained were 54.5 per cent and 3.6 per cent. We therefore see that the highest value of the reduction corresponds with the lowest quantity of hypochlorite. We must therefore conclude that, in some way or another, the action of the chromate retards the reduction at the cathode.

It thus appeared to be possible that an addition of chromate would also favour the production of bromates and iodates by electrolysis. As we already know (*Zeit. f. Elekt.*, 1897, p. 474; *Journ. f. Prakt. Chemie*, 1897, lvi., 353) those salts are again reduced by the current to the state of bromides and iodides in such a way that after a little while the return becomes very low. The preceding supposition is, in fact, found to be perfectly true. Without wishing to here record all our unsuccessful experiments, we will quote two carried on for a long time under conditions that we considered to be very favourable.

The experiments were carried out in a glass vessel of 120 c.c. capacity, closed like the preceding one. Two strips of platinum of 10 sq. c.m. area, about 1 c.m. apart, served as electrodes. The intensity of the current was 1 ampère.

EXPERIMENT IV.—The Solution (100 c.c.) contained 20 grms. KI, 1 gm. KOH, and 0.18 gm. K_2CrO_4 .

Temperature, 40°. $D_a = D_c = 0.1$ amp./sq. c.m.
 Tension = 3.3 to 3.7 volts.

Time. Hours.	Return from current. Per cent.	Reduction. Per cent.	Decomposition of water. Per cent.
1	98.7	9.8	0.5
2	97.5	1.4	1.1
4	99.1	0.9	0.0
15	96.7	0.0	3.3
16	91.0	1.8	7.2
17	91.4	1.3	7.3
19	81.7	0.4	17.9
21	27.3	0.6	72.1
22	9.1	4.3	86.8

There were deposited 26.18 grms. of copper in the voltmeter, corresponding to 6.6 grms. O_2 . By crystallisation we obtained 21.5 grms. of KIO_3 , corresponding to 4.823 grms. O_2 , and the solution still contained 0.8258 gm. O_2 , or a total of 5.6488 grms.; that is to say, 85.6 per cent of the theoretical return. If we neglect the two last hours, we obtain 97 per cent of the theoretical return. Theoretically, 20 grms. KI should be entirely transformed into KIO_3 at the end of 19.3 hours. We obtained 97.7 per cent of iodide oxidised to iodate.

EXPERIMENT V.—The Solution contained 20 per Cent of KBr and 0.18 per Cent of K_2CrO_4 .

Temperature = 32–36°. $D_a = D_c = 0.1$ amp./sq. c.m.
 Tension = 2.5–4.1 volts.

Time. Hours.	Return from current. Per cent.	Reduction. Per cent.	Decomposition of water. Per cent.
$\frac{1}{2}$	97.3	2.1	0.6
3	94.8	2.5	2.7
13	93.7	4.1	2.2
14	90.6	6.1	3.5
19	93.1	3.7	3.2
21	94.5	3.3	2.2
23	90.7	4.4	4.9
25	90.2	3.9	5.9
26	91.8	3.4	4.8
28	82.5	3.1	4.4
30	64.2	3.1	2.7

In the voltmeter were deposited 34.75 grms. of copper, corresponding to 8.77 grms. of oxygen. On crystallisa-

tion we obtained 19.85 grms. of $KBrO_3$, corresponding to 0.706 gm. of O_2 . There remained in solution 2.1752 grms. of O_2 . This makes a total of 7.8812 grms. O_2 , or 89 per cent of the theoretical return. In this case, again, the return from the first twenty-one hours gives a mean of 94 per cent of the theoretical return. Theoretically, the 20 grms. of Br ought to have been oxidised into $KBrO_3$ after 26.9 hours. We obtained 37.6 per cent of the bromide oxidised to bromate.

We obtained just as good results with soda salts, and on a much larger scale, using 500 c.c. of a 20 per cent solution. We also made a certain number of experiments to determine the most favourable conditions from several different points of view.

To obtain a pure product it is necessary to use a platinum anode; with a carbon anode the solution becomes coloured brown, as also are the crystals which are formed. Powdered carbon is also deposited; this is removed mechanically from the electrodes—the salts crystallising on the surface of the carbon appear to disintegrate it. As a cathode, we may use platinum, iron, nickel, or copper; lead and zinc are not suitable. The following figures give the reduction in the electrolysis of a neutral solution of NaBr with a cathode formed of these metals:—

EXPERIMENT VI.

Metal of the cathode.	Reduction, Per cent.	
	Maximum.	Minimum.
Platinum	0.2	2.9
Nickel	2.1	2.5
Iron	2.6	3.9
Copper	2.9	3.8
Lead	5.6	15.5
Zinc	20.0	30.8

As for the composition of the electrolyte, an addition of an alkali increases the quantity of water decomposed in the case of bromides and chlorides, but it has no influence on the return with iodides; this was to be expected in view of the values of the potential of discharge of the ions of hydroxyl and of the halogens.

It is important, at least with iodides and bromides, to continually stir the electrolyte, or otherwise the salt in crystallising will entangle some of the halogen.

Concentrated or dilute solutions are equally good for electrolysis. In fact, we only notice a diminution in the return when the solution is very dilute indeed.

We also tried making the proportion of chromate variable. If it is increased the decomposition of water increases slowly, if it is diminished it is the reduction that is increased.

The salts in which the chromium is in the state of oxide play the same part as the chromate; they are oxidised by the current. In any case, at the end of the experiment, we do not find that the proportion of chromic acid has varied.

As a general rule the experiments are carried on at a high temperature, so as to diminish the voltage. With chlorides, it must be remembered that below 25° we obtain a notable proportion of perchlorate. With iodides and bromides the return is equally good, hot or cold, as neither the bromates nor the iodates can be oxidised by electrolysis, even at a very low temperature. In such a case the temperature should not exceed 50°, as at a higher temperature the reduction is stronger.

The density of the current may be varied between wide limits, as shown in the experiments. It is difficult to explain the influence of the chromate.

Whatever it may be, it is noticed that after the experiment the cathode has a peculiar appearance, which is not that of clean platinum; this is caused by the chromium. There are two possible cases; it may be that the cathode becomes covered with a thin layer of chromic hydrate, which acts like the lime which forms a diaphragm interfering with the reduction, in the electrolysis of solutions

of chloride of calcium (*Zeits. f. Elektr.*, 1898, No. 20). This would explain why the voltage was higher for solutions containing chromate, although this might also be explained by a variation in the polarisation of the hydrogen. But the fact that the hypochlorite rapidly oxidises the chromic hydrate into chromic acid is contrary to this hypothesis; it would then be necessary for the hydrogen to reduce CrO_3 to Cr_2O_3 , in the same way that NaOCl oxidises Cr_2O_3 to CrO_3 , and in this case the value of the reduction would not give any indication.

It might also be possible for an alloy of chromium to be formed on the surface of the cathode. It is an experimental fact (*Zeits. f. Elektr.*, 1896, No. 16) that the alkaline chlorates undergo reduction, more or less, according to the metal used as cathode, and it may be imagined that the metallic chromium formed on the surface of the cathode would interfere with reduction. As a matter of fact, the metals which interfere with the reduction have a close, dead-white appearance at the end of the electrolysis, while zinc and lead become covered with an easily-removed porous material. This phenomenon might perhaps be cleared up, if we admit that all the metals which form a porous non-compact alloy with chromium during electrolysis are unable to prevent reduction.* We may here mention that the salts of manganese have not the same action.

Finally we would remark that, to all appearance, an addition of chromate is an advantage in every case when the products of oxidation at the anode require to be protected against reduction. — *Zeitschrift für Elektrochemie*, v., p. 469.

THE DETERMINATION OF ANTIMONY IN ORES.†

By THOMAS BROWN, Jun.

(Concluded from p. 179).

1. *The Soluble Ores.*—For the "soluble ores" 1 grm., which has been finely pulverised in an agate mortar, is treated in a No. 3 beaker with 25 c.c. concentrated hydrochloric acid, covered and boiled on a plate or over a flame until apparently decomposed and the solution is not more than 15 c.c. in bulk. About 2 grms. of tartaric acid are added, and as soon as that is dissolved about 4 to 6 drops of concentrated nitric acid, and the whole is boiled for a minute or so more. This last addition causes a violent reaction and a more complete decomposition. The beaker is now removed from the source of heat, the cover and sides washed down, the insoluble residue filtered out, and the filtrate and washings diluted in bulk to about 250 c.c. A steady stream of hydrogen sulphide gas is now run through the solution for about an hour until it is thoroughly saturated and the antimony thus precipitated as the amorphous orange-coloured sulphide (Sb_2S_3).

To insure a complete precipitation this is gently warmed in order to convert any basic chloride into sulphide, and then allowed to stand an hour or so in the cold before filtering. The filtrate will then be perfectly clear, and not deposit additional antimony upon standing or upon further treatment with hydrogen sulphide gas. Should lead or other impurities of the fifth group have been found by the preliminary qualitative tests, after filtering and washing the precipitate with cold water it is washed back into the beaker in which it was precipitated, and treated with ammonium sulphide in such excess that with the aid of heat the antimony precipitate completely dissolves. The solution is then run back through the same filter, caught in a clean beaker, and the filter thoroughly washed

with hot water. The solution and washings are acidified in slight excess with hydrochloric acid, re-precipitating the antimony sulphide, diluted to about the same bulk as before (250 c.c.), allowed to stand a few minutes to settle, and then filtered. In the black sulphide residue remaining on the filter representing the impurities of the fifth group, the lead may now be determined by placing the filter containing this precipitate into a beaker, treating with nitric acid and boiling, adding ammonia in excess, then acetic acid in excess, filtering, re-precipitating the lead as chromate, and weighing it thus on a Gooch crucible or balanced filter-papers.

The antimony sulphide precipitate, whether precipitated but once or re-precipitated for purification, is now washed well upon a large, plaited, balanced filter, with cold water, and dried in an air-bath at 110°C . for two hours or more to constant weight. After removal, and as soon as cold, the weight of the dried precipitate is taken, which consists of antimonious sulphide (Sb_2S_3) mixed with a small amount of free sulphur.

The following procedure has been found both rapid and accurate for weighing this precipitate. A German corrugated filter, 15 c.m. in diameter, is used. Two are selected which lay beside one another in the same pack, and which from long impact contain practically the same amount of moisture. They are balanced by cutting down the heavier one. Upon the unaltered one the precipitate is filtered, the other accompanying it in the drying oven and as a counterpoise in weighing. When the weight of the precipitate has thus been determined, it is carefully scraped from the paper and powdered, and mixed well by grinding in a small glass mortar. A certain amount of this (5/10ths grm.) is weighed off into a platinum boat, this introduced into a glass combustion-tube, and the free sulphur driven off in a stream of carbon dioxide. From the weight of the resulting black anhydrous antimonious sulphide so obtained on a weighed amount of the dried precipitate, its total weight thus treated can easily be calculated, and it is then simply a matter of calculation to determine the total amount of antimony present. $\text{Sb}_2\text{S}_3 \times 0.7177 = \text{Sb}$.

The combustion requires in all from twelve to fifteen minutes, and, if carefully conducted with the following precaution, very little loss if any at all occurs. Arsenic if present would be volatilised. (a.) A steady stream of gas should be passing through the tube when the flame is applied underneath the boat, and should continue so with as little variation as possible until the end of the operation. Should this not be the case, a flame would at first play over the surface of the contents of the boat, causing oxidation apparent to the eye when removed from the tube by a whitening of the surface and consequently a loss in weight. (b.) The heating of the boat in the tube should be accomplished gradually. At first a gentle heat is applied until all the sulphur has apparently been driven off, and increased towards the end of the operation. (c.) The tube should be cleaned of sublimed sulphur by heating before each and every determination. After weighing the boat and contents it is well to treat again for additional loss in weight, which is rarely found if the operation has been conducted as described.

2. *The Practically Insoluble Ores.*—The important point here is the decomposition of the ore which is accomplished by fusion. One grm. of the finely-powdered ore is mixed with 8 to 10 parts of a flux composed of equal parts of flowers of sulphur and sodium carbonate, introduced into a porcelain crucible (capacity 40 c.c.), and in addition the mixture is covered with a thin layer of the flux. The covered crucible is introduced into the opening of a muffle that is of a bright red heat, and is cautiously heated to fusion for about ten minutes. The heat applied at first should be of such an intensity that sulphur flames are barely seen escaping around the edge of the lid; after they cease it is somewhat increased by pushing the crucible a few inches farther back in the muffle. At no time should the crucible become heated to more than per-

* Possibly these facts are in accordance with those observed by Bröglig and Haber (*Deutsch. Ch. Ges.*, 1898, xv., p. 2741).

† From the *Journal of the American Chemical Society*, vol. xxi., No. 9.

ceptible incandescence on the side facing the source of heat, and during the operation it should be occasionally turned with a pair of tongs to insure an even heating and consequently a complete decomposition. The colour of the melt when cold should be green, not yellow, and likewise the solution of the same, due to the sulphide of iron present. A suggestion of a yellow colour particularly in the solution indicates an incomplete decomposition of the ore, and but a partial change of the antimony into the soluble sodium sulphantimonate, which consequently necessitates a repetition of the fusion.

A successful fusion, owing to the ready volatility of antimony at a comparatively low degree of heat, is rather a delicate thing and difficult to accomplish, requiring constant care and judgment only gained by experience. With the statement that it is possible to thoroughly decompose such an ore by fusing over a candle-flame, the writer is compelled to differ, having frequently found that a fusion made at a seemingly alarming degree of heat gave, when dissolved, a yellow solution in which the antimony when determined was found to be lower than that of a duplicate sample which had been treated to a higher degree of heat. It is, therefore, better to treat in excess than not to fuse enough; for should there be a slight loss by volatilisation, this would in a measure be counterbalanced by the small amount of impurities, such as silica, obtained from the action of the flux on the crucible and on the silica of the ore, and consequently thrown down by the acid and weighed with the antimony sulphide precipitate. The degree of heat used, however, should scarcely affect the glaze of the crucible. When the fusion has thus been satisfactorily accomplished, and when cool, it is dissolved in hot water, which takes but a few minutes; the suspended precipitate of iron sulphide and sulphides of the metals of the fourth group, if present, filtered off, and the antimony precipitated by adding a slight excess of hydrochloric acid to the filtrate. After stirring and allowing to stand a few minutes to settle, the precipitated antimonious sulphide (Sb_2S_3), mixed with more or less free sulphur, is filtered off upon a balanced filter, and so determined as before, being ultimately weighed when removed from the combustion-tube as antimonous sulphide (Sb_2O_3).

3. *The Partially Soluble Ores.*—These ores require a double treatment, that is, they are first treated as for soluble ores and the antimony determined in the acid solution, and the residue—remaining on the filter which contains the undissolved oxide—is subjected to a fusion as for oxide ores. This filter-paper is placed in the bottom of a porcelain crucible and covered well with flux, so that some comes in direct contact with its contents. It is then fused as directed. In dissolving, pieces of charred paper may possibly be found, which are, however, filtered out together with the insoluble matter. The amount of antimony so present is determined as before.

Most Mexican so-called sulphide ores exported are really oxysulphides, being mixtures of sulphide with a small amount of oxide which has not been separated in the sorting: these ores consequently require this double treatment. The following is a list of results obtained in using these methods upon the previously mentioned varieties of Mexican ores, and gives in the case of oxysulphides the soluble and insoluble antimony found. In the last column will also be found the results by the fire assay, which is extensively used on oxide ores for prospecting work, and also for large shipments when the "wet assay" is to be made later at their destination. It is figured by the dealers that the wet assay of a 60 per cent ore will go 6 per cent higher than the dry or fire assay. That there are exceptions to this will be seen in Nos. 5, 8, and 12 of the table. No. 5 is the senarmonite ore, the complete analysis of which has already been given, while Nos. 8 and 12 are quite insoluble under the acid treatment, leading to the supposition that they are cervantite ores of the composition Sb_2O_4 . It has also been observed that certain grades of oxide ores give higher results by fire

assay than other grades, which is considered due to their ultimate composition, of which very little is so far known. The widely different and extremely low results obtained by fire assay upon sulphide ores makes them no criterion upon which to judge of the actual antimony present, and so for this class of ores it is falling into disuse.

No.	Class of ore.	Soluble Sb.	Insol. Sb.	Total Sb.	Fire assay.
1.	Sulphide ..	67.4	—	67.4	—
2.	" ..	28.5	—	28.5	—
3.	Oxysulphide .	61.6	5.1	66.7	48.0
4.	" ..	63.3	6.7	70.0	45.0
5.	Oxide ..	70.7	3.1	73.8	72.8
6.	" ..	—	—	71.7	65.0
7.	" ..	—	—	66.1	59.0
8.	" ..	—	—	63.9	61.8
9.	" ..	—	—	55.8	49.0
10.	" ..	—	—	49.0	43.0
11.	" ..	—	—	48.3	43.0
12.	" ..	—	—	46.4	44.4

The fire assay referred to consists of the reduction of the contents of the ore to the metallic state by fusion with potassium cyanide, and while it is known that it is possible to obtain higher results by the use of other mixed fluxes together with a treatment for a longer time at a lower heat, this cyanide reduction remains the accepted method in trade. It is performed as follows:—Five grms. of the powdered ore is mixed with 12 parts of potassium cyanide, placed in a 10 gm. clay crucible, and covered with salt. The fusion is made in a muffle at a bright red heat, allowing it to remain there thirteen minutes. When removed it is thoroughly shaken to collect the globules into one metallic button, and allowed to cool. The crucible is broken, and the resulting button carefully broken from the slag and weighed.

In conclusion the writer desires to express his obligation both to Mr. M. Elasser and to Mr. Ferdinand McCann, for their kind assistance in furnishing him with suggestions, data, &c., without which this paper would not have been written.

ON THE DETERMINATION OF SULPHURIC ACID IN THE PRESENCE OF IRON:

A NOTE UPON

SOLID SOLUTIONS, AND THE HYDROLYSIS OF CHROMIC AND FERRIC SALTS.*

By THEODORE WILLIAM RICHARDS.

WITHIN the past year appeared three interesting articles by Küster and Thiel (*Z. Anorg. Chem.*, 1899, xix., 97; 1899, xxi., 73; 1900, xxii., 424), concerning several methods of precipitating baric sulphate free from iron when that element has been present in the solution. One of the methods which they have proposed is an excellent addition to our always imperfect analytical repertory, and the chemical world owes them a debt for the ingenious although exceedingly simple suggestion.

While not wishing in the least to detract from the merit and interest of this work, I feel that attention should be called to several omissions in their paper, especially those which concern theoretical considerations involved in previous work upon the subject.

In their first paper, where the admirable analytical device is explained, Küster and Thiel ascribe the "occlusion," of iron to the presence of the ferric ion. It is interesting that this idea, which they themselves have since shown to be false, should have led them to the

* Contributions from the Chemical Laboratory of Harvard College. A part of this paper appeared in *Proc. Amer. Acad.*, 1900 xxv., 377, and it is published in full in *Zeit. Anorg. Chem.*

desired goal. The circumstance might be taken as an argument in favour of the proposition that even an incorrect idea is better than none. In a reference to this paper, Ostwald (*Z. Phys. Chem.*, 1899, xxix., 340), points out that the occlusion is in all probability due not to the ferric ion, but rather to a molecular complex; and in their last paper, Küster and Thiel describe experiments which prove beyond much doubt the correctness of Ostwald's suggestion. Oddly enough, however, they still cling, in their summing up of the matter, to the statement that the ferric ion is the essential agent.

It is curious also that they should have overlooked the following statement in a paper published over ten years ago by Professor Jannasch and myself. In speaking of the cause of the phenomenon under consideration, we said:—"Es lässt sich unmittelbar annehmen, dass das Eisen als eine Doppelverbindung mit Baryum als Baryum-Ferrisulphat gefällt wird, welches wahrscheinlich ein Molekül gebundenes Wasser (sogen. Constitutionswasser) enthält" (*Jannasch and Richards, Journ. Prakt. Chem.*, 1889, [2], xxxix., 321). Küster and Thiel have offered new arguments which they consider as being in favour of the first part of this incomplete proposition, without appearing to recognise that the proposition is not itself new. They have moreover ascribed an arbitrary formula to the substance, while we did not feel prepared either to assume its exact nature or to explain the mechanism of its occlusion.

Three years after this publication Schneider described some interesting experiments in which evidence was given that the occlusion of the double or complex compound is a variety of solid solution (*E. A. Schneider, Zeit. Phys. Chem.*, 1892, x., 425). The idea was new at the time, and did not meet with general favour; but a knowledge of the work would have saved Küster and Thiel trouble.

In 1894 (*T. S. Gladding, Journ. Amer. Chem. Soc.*, 1894, xvi., 398; 1895, xvii., 397), after the passing of two more years, Gladding published a modification of Lunge's method of precipitating baric sulphate free from iron, which is the most convenient of any which had appeared up to that time. He precipitated the iron with ammonia, filtered without especial washing, acidified the filtrate, added an excess of baric chloride, and then collected on one filter both the main mass of the baric sulphate and the small amount of the same substance which he obtained from the ferric hydroxide. The chief difference between this method and the method of Küster and Thiel is the fact that the latter pointed out the uselessness of filtering off the ferric hydroxide before adding the baric chloride. It is quite probable, however, that Küster and Thiel did not know of Gladding's work, and hence independently devised the whole process.

Let us consider for a moment the nature and cause of this kind of occlusion. In the first place it must be distinguished sharply from the mechanical retention of mother-liquor in minute cells which all crystalline precipitates exhibit. Even large crystals rarely contain cells of included mother-liquor plentiful enough to increase their weight by more than the fraction of a per cent; and this impurity is of course chiefly water. It is easy to test the magnitude of this inclusion by precipitating such a substance as calcic carbonate from a solution containing a large quantity of some easily identified substance such as sodic chloride. Mr. R. P. Cushing kindly made a number of such experiments for me, and found that not even from a saturated solution of salt did more than 0.1 per cent of the precipitate consist of sodic chloride. Of course this value fixes the maximum, for some of the substance may well have been occluded instead of included.

Very different from the mechanical process of inclusion is the behaviour of baric sulphate. Here the impurities may amount to several per cent, and the foreign material is disseminated equally throughout the mass. The experiments of Schneider show that the amount of the occlusion is greater as the concentration of the impurity in the solution increases, although not in direct proportion.

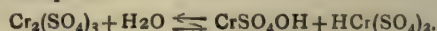
It is very clear that we are dealing here with a special case of the distribution law; Küster and Thiel evidently thought of this possibility, but they did not amplify the idea. The distribution can take place only at the moment of precipitation, because afterwards the rigidity of the solid prevents free motion. In the present paper I have retained the name occlusion for this phenomenon because no other term seems to be applicable. There is indeed a certain analogy between the occlusion of hydrogen in palladium and the dissemination of a solute out of a solution into a solid; and since the name gives rise to no misunderstanding it will answer its purpose.

Obviously the study of the distribution law in other cases should throw light upon this one by analogy. When hydrochloric acid is distributed between its aqueous solution and the vapour phase, the concentration of the undissociated part alone is concerned in the distribution, because ions can exist only in the solution. In the same way, when a moderately strong acid is distributed between water and ether, only the undissociated part of the acid comes into play, because ether does not cause important dissociation. From these analogies one might infer that the group which is concerned in cases of concomitant precipitation are not ions, but rather electrically neutral complexes. The inference is not a perfectly safe one, for little is known about the possible degree of dissociation in solids; but experimental evidence is at hand to support this view. In 1894 Richards and Parker made the observation that the occlusion of baric chloride by baric sulphate is much increased by the previous addition of hydrochloric acid to the solution of baric chloride (*Proc. Amer. Acad.*, 1894, xxxi., 74; *Zeit. Anorg. Chem.*, 1895, viii., 420). For example, the addition of 20 c.c. of strong hydrochloric acid caused almost twice as much occlusion as the addition of 10 c.c. in another otherwise similar case. The conditions attendant upon mixing two liquids are so uncertain that it is unsafe to attempt the quantitative interpretation of the relationship; but qualitatively this result is wholly in accord with the law of mass action, provided that the undissociated group is supposed to be the one concerned.

The nature of the electrically neutral group with which we have to do in the present case is less easy to imagine. Küster and Thiel assume that it is $\text{Ba}[\text{Fe}(\text{SO}_4)_2]_2$; but this is evidently an unsafe assumption. The analogy to the case of chromium which they quote is an excellent point, but they apply their useful analogy in an incomplete fashion.

Recoura (*Amer. Chem. Phys.*, [4], vii., 497), and Whitney (*Zeit. Phys. Chem.*, 1896, xx., 40), and others have shown that a "modified" green solution of chromic sulphate certainly contains an acid. In other words, it is hydrolysed, and must likewise contain a basic complex. It has also been shown that in the presence of much free sulphuric acid, a complex of an opposite nature, chromosulphuric acid, $\text{H}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3$, is formed. None of these investigators have completed the explanation by the following hypothesis, however.

As the acid is set free by the progressing hydrolysis of the normal violet chromic salt, this acid must simultaneously cause the formation of chromosulphuric acid. In short, a reaction somewhat like the following must take place:—



Perhaps this statement does not exactly represent the proportions; but nevertheless it accords with the quantitative results of Whitney and Recoura. It will be remembered that they found each molecule of chromic salt capable of yielding one replaceable hydrogen, and also that only a third of the sulphate was capable of immediate precipitation. This explanation is much simpler than the complicated assumptions of Recoura.

According to our first hypothesis that compound which is most dissociated should be least occluded by baric sulphate. Now the conductivity measurements of Whitney

show that the acid complex is far more dissociated than the basic one; hence I am inclined to ascribe the occlusion chiefly to the basic substance. This interpretation is diametrically opposite to the interpretation of Küster and Thiel.

Nevertheless, among the results of Küster and Thiel's work, we find other arguments indicating the basic nature of the occluded body. On pages 439—440 of their third paper they point out that the addition of acid diminishes very much the occlusion of the iron complex. This is wholly consistent with the present thesis: for (according to the Mass Law) the addition of acid must diminish the concentration of the basic complex in the solution, and hence (according to the distribution law) the amount which finds its way into the solid. It is true that this argument is somewhat diminished in force by two circumstances: first, because Küster and Thiel have not here considered the fact that hydrochloric acid increases the weight of the precipitate by introducing into it more baric chloride; and second, because the addition of hydrochloric acid undoubtedly causes a chloride-complex which is not occluded to nearly so great an extent as the sulphate-complex by the baric sulphate. In order really to study the effect of the hydrogen ion one should not rely simply upon the total weight of the mixed precipitate, but should actually determine the amount of iron present in the precipitate and compare it with the amount present in a precipitate obtained from a solution containing the same amount of iron and an amount of sodic chloride equivalent to the hydrochloric acid used in the first case. In spite of these objections, however, the effect observed by Küster and Thiel is so great that one must ascribe a portion of it to the action of the hydrogen ion, and hence, according to Whitney and Recoura, infer the substance concerned to be a basic complex. Küster and Thiel offered no explanation for the action of the hydrogen ion.

Again, Küster and Thiel point out (pp. 437—438) that the hydrolysis caused by dilution prevents the addition of much water from causing as considerable a decrease in the absorbed material as would otherwise have been expected. This is equivalent to saying that the complex which is concerned is a basic one; for the hydrolysis of course involves the ionisation of hydrogen.

Yet another, although less cogent, argument in favour of the basic nature of the complex is the fact that Jannasch and I found the impure baric sulphate to be capable of retaining about 3 per cent of water at 250°. While it is not impossible that this should be at least in part simply held in minute cells or as crystal-water, one is inclined to ascribe part of it to hydroxyl existing in the precipitate. It may well be, however, that the extra water is simply dissolved in the precipitate, as other undissociated substances are dissolved by baric sulphate. This tendency to dissolve water may be the reason why many precipitates require prolonged ignition in order to attain constant weight.

Over a year ago I was attracted by the well known occlusion of green chromic sulphate by baric sulphate, into beginning a study of the subject of occlusion with the help of this phenomenon. Chromium was selected instead of iron because its complex is more stable and has been more thoroughly studied. The research was begun by Mr. R. P. Cushing, and is being continued by Mr. F. Bonnet. Since the precipitated baric sulphate is green, one must infer immediately that the green modification (or complex) is responsible for the occlusion. The work is not yet ready for publication, but our data agree well with those of Küster and Thiel, while our explanation accords with that given in the present paper. We are also studying aluminum sulphate, which likewise seems to form a complex very considerably occluded by baric sulphate; although this fact does not seem to be generally known (compare Peckham, *Journ. Amer. Chem. Soc.*, 1899, *xxi.*, 772).

This paper is intended to serve as an introduction to two other papers upon specific cases of occlusion. The

chief points upon which emphasis is desired are the following:—

1. Occlusion from solutions differs from inclusion by being a more intimate and a less mechanical mixture.

2. Occlusion differs from adsorption in concerning the whole mass of the precipitate, and not merely its surface. Hence after a precipitate is once formed occlusion takes place only with extreme slowness, because of the rigidity of solids. New evidence of this will be given in one of the following papers.

3. Different precipitates have almost as widely varying powers of occluding other substances as different liquids have widely varying powers of dissolving other substances. The property is no more to be predicted than the power of dissolving.

4. The process of occlusion is probably the distribution of an electrically neutral simple substance or complex between the solution itself and the solid at the moment of its formation within the solution. Hence any change in the substances present in the solution which tends to diminish the concentration in the solution of the group under consideration, tends to diminish the amount occluded.

5. The nature of the groups which are occluded in the cases of iron, chromium, and aluminum is not yet determined, but they are probably basic in nature, and identical with the complexes of Recoura and Whitney.

6. Green chromic sulphate solution apparently contains not only a basic complex, but also a chromosulphuric acid, which is not precipitated by baric salts. This compound is only slightly occluded by baric sulphate because it is much dissociated. Its effect is simply to delay the precipitation of baric sulphate, a consequence which Küster and Thiel have correctly interpreted. The whole subject is now being further studied here, for the hypotheses are capable of further experimental treatment.

Harvard University, Cambridge, Mass.,
February 2, 1900.

THE ACTION OF AMMONIUM CHLORIDE UPON ANALCITE AND LEUCITE.

By F. W. CLARKE and GEORGE STEIGER.

In a recent paper (*Amer. Journ. Sci.*, October, 1899), upon the constitution of certain silicates, we showed that analcite, when heated with ammonium chloride, gave up a part of its soda, and absorbed ammonia to an appreciable extent. This result was so remarkable that it seemed to demand further investigation, upon material of different origin, and with variation in the details. The new experiments, which have led to highly interesting consequences, are now to be described.

The analcite previously studied was from Nova Scotia. To the kindness of President Regis Chauvenet, of the State School of Mines, we are indebted for a liberal supply of well-crystallised material from North Table Mountain, near Golden, Colorado, of which a uniform sample of about 80 grms. was prepared. Upon this sample the present series of experiments has been conducted. Analysis of the analcite gave the following results:—

Analysis.	Water by fractions.
SiO ₂ 55.72	At 100° 0.13
Al ₂ O ₃ 23.06	„ 180° 0.75
CaO 0.17	„ 260° 2.44
Na ₂ O 12.46	„ 300° 1.28
H ₂ O at 100° .. 0.13	„ 350° 1.76
H ₂ O above 100° 8.26	„ redness 2.03
99.80	Total .. 8.39

Above a low red heat no further loss of weight was observed. Upon boiling the powdered mineral for fifteen minutes with a 25 per cent solution of sodium carbonate, 0.45 per cent of silica was dissolved. After ignition, 0.57 per cent was soluble, which is practically the same amount. No silica was split off by heating.

The experiments with ammonium chloride fall into two series. The first of these was conducted precisely as in our former investigation, by grinding the powdered mineral into an intimate mixture with four times its weight of chloride, and heating in an open crucible. In three cases the material, after volatilisation of the ammonium chloride, was re-ground with a fresh amount of the salt, and then heated again. The temperature and duration of the experiments was purposely somewhat varied. After heating, the material was leached out with water, the sodium chloride which had been formed was estimated, and in the residue the fixed ammonia was determined.

In this series there were four experiments, with results as follows:—

	Hours heated.	Temperature.	Soda removed.	Ammonia in residue.
A	28	300°	4.75	2.04
B	8½	350°	6.36	2.88
C	26	350°	3.76	1.72
D	5	340° to 380°	6.70	2.85

In our work upon the analcite from Nova Scotia the ammonia retained by the leached residue ranged from 2.03 to 2.36 per cent, while the extracted soda varied from 5.07 to 6.10. In two of the new experiments these figures are perceptibly exceeded, and they represent the shortest duration of heating. Prolonged heating seems to be undesirable, and to undo a part of the reaction which has taken place; otherwise the results obtained are of the same order as their predecessors. About one-half of the soda in the analcite is converted into chloride, while variable ammonia is retained.

In the second series of experiments a sealed tube was substituted for the open crucible. The powdered analcite was intimately ground with four times its weight of ammonium chloride, as before, and then heated to 350° in a tube furnace for from four to eleven hours. Under these conditions practically the whole of the soda in the mineral was converted into sodium chloride, while all of the liberated ammonia was absorbed by the residual silicate. Upon leaching the contents of the tube with water, to remove sodium and ammonium chlorides, a residue was obtained which exhibited constant composition whether dried at 100° or at the ordinary temperature of the air. Three samples of the residue were prepared and analysed; other samples were partially examined and used for subsidiary experiments. The three analyses, lettered for future reference, were as follows, the analcite itself being included in the table for comparison.

	Analcite.	Residue A.	Residue B.	Residue C.
SiO ₂	55.72	61.93	61.68	61.79
Al ₂ O ₃	23.06	25.21	25.33	25.24
CaO	0.17	—	—	—
Na ₂ O	12.46	0.40	0.22	0.28
NH ₃	—	7.23	6.95	7.71
H ₂ O	8.39	4.50	4.91	5.01
	99.80	99.27	99.09	100.03

Residue C was prepared with the greatest care, and was air-dried. Exposed over sulphuric acid in a vacuum desiccator for fourteen days, it lost in weight only 0.08 per cent. Tested for chlorine, only a slight trace could be recognised, but upon boiling for fifteen minutes with sodium carbonate solution it yielded 1.97 of soluble silica. After ignition only 1.70 of silica was soluble, or somewhat less than before. Upon heating at constant weight at 300°, only 0.46 per cent was lost; but at 350° it slowly decomposed, giving off ammonia. At 300° the compound is stable.

The 0.28 per cent of soda remaining in residue C may be regarded as representing unaltered analcite,—doubtless coarser particles which escaped complete transformation. It corresponds to 1.98 per cent of analcite, which, together with the 1.97 of soluble silica, and the 0.46 of water lost below 300°, may be deducted from the substance in order to obtain the composition of the definite compound. The latter amounts to 94.72 per cent of the total residue, and agrees very nearly in composition with the formula $2\text{NH}_3 \cdot \text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$. Re-calculating the 94.72 of residue to 100 per cent, we get the following comparison between analysis and theory:—

	Found.	Calculated.
SiO ₂	61.07	60.92
Al ₂ O ₃	26.15	25.88
NH ₃	8.14	8.63
H ₂ O	4.64	4.57
	100.00	100.00

Written in rational form the compound becomes equivalent to an anhydrous ammonium analcite, $\text{NH}_4\text{AlSi}_2\text{O}_6$; that is, analcite in which sodium has been replaced by ammonium. From this point of view the reaction between analcite and ammonium chloride becomes a simple case of double decomposition, and is perfectly intelligible. To establish this conclusion, however, corroborative experiments were necessary.

In the first place, the observed equivalency between the sodium lost and the ammonia gained might be due to a mere coincidence, and so far be illusory. One atom of sodium, taking chlorine from ammonium chloride, liberates one molecule of ammonia, the amount which the analcite residue has retained. Suppose more ammonia were present,—could it be absorbed?

To answer this question another tube was prepared, with the usual mixture of analcite and ammonium chloride. This was covered by a loose plug of glass-wool, in front of which we placed enough pure lime to liberate about double the normal amount of ammonia. The tube was then sealed, and heated to 350° as in the previous experiments. Upon opening the tube, a strong outrush of ammonia was noticed; but in the leached and thoroughly washed residue only 7.52 per cent of ammonia was found. This quantity agrees with that from the previous samples, and shows that the limit of the reaction has been practically reached. One molecule of ammonia is retained, and no more.

Still another experiment was tried upon a portion of the residue marked C. If the compound is really an ammonium salt, it should be decomposable by caustic soda in such a way as to reverse the reaction by which it had been obtained. The substance, however, is very insoluble, so that the reaction takes place slowly. To phenol-phthalein it is absolutely neutral, and with Nessler's reagent it reacts only after long standing.

To settle the question a weighed portion of the compound was boiled in a distilling flask with a 10 per cent solution of sodium hydroxide, to which water was added from time to time. The distillate was collected in a tube containing aqueous hydrochloric acid, and the ammonia which passed over was weighed, ultimately as chloroplatinate. By four hours boiling 6.90 per cent of ammonia was driven off and determined; and the residue remaining in the flask, after washing until no alkaline reaction could be detected in the wash-water, was examined for soda, of which 10.41 per cent was found. The anticipated reaction had taken place, although not completely; it was enough, however, to confirm our opinion, and to establish the nature of the new compound beyond reasonable doubt. Other confirmation was obtained later, from the study of leucite.

The foregoing paragraphs now enable us to understand a phenomenon which we observed in our work with the open crucible. In that case a partial reaction takes place between the analcite and the ammonium chloride, pro-

ducing, as in the sealed tube, a mixture of an ammonium aluminosilicate with sodium chloride, the two substances being separable by leaching. But if, instead of leaching, the mixture be heated to full redness, ammonium chloride is re-formed and given off, leaving a residue which contains little or no sodium chloride, and is wholly insoluble, or almost so, in water. That is, the reaction which occurs at 350° is reversed at the higher temperature, and anhydrous analcite, or an isomer of it, is regenerated. Ammonium and sodium again change places, and the original state of molecular equilibrium is restored.

What, now, is the nature of the product obtained in the open crucible, after sodium chloride has been removed? It is a definite, intermediate compound, or an indeterminate mixture? In our former paper we adopted the first of these alternatives, and assigned to the substance the formula $H_2Na_2Al_4Si_8O_{24}.NH_3$. In this expression we were influenced by the researches of Friedel, who had shown that ammonia could in part replace the "zeolitic" water of analcite; but it now appears that the phenomenon observed by him is quite distinct from that discovered by us, and, indeed, of an entirely different order. We may therefore, in accordance with our new data, rearrange the formula; transforming it to that of an ammonium salt, $HNH_2NH_4Al_4Si_8O_{24}$, the agreement with the analytical figures being approximate only. The results obtained are not sharp enough for certainty.

This product we are now inclined to regard as a mixture, although it is not strictly intermediate between analcite and its final ammonium derivative. Only half of the eliminated sodium has been replaced by ammonium, while hydrogen, or water, makes up the deficiency. It seems probable that the reaction in the sealed tube and that in the open crucible are at first essentially the same; but that in the latter case secondary reactions follow which cause the variations in the final results. In the sealed tube, the element of pressure comes into play, and the reaction is complete. In the open crucible, pressure is lacking; some ammonia escapes fixation and reacts upon a part of the sodium chloride which was at first formed; hence the composition of the leached residue is essentially modified. This residue may be a definite compound; but the case in its favour is unproved, and the presumption is rather against it.

Between analcite and leucite the closest analogies have long been recognised. The two minerals have similar composition, they resemble each other in crystalline form, and they yield, upon alteration, products of the same order. Recently also, analcite, like leucite, has been identified as a not uncommon constituent of volcanic rocks; analcite-basalt being a good example. In view of these resemblances, it was plainly desirable to compare the minerals by means of the ammonium chloride reaction; a task which has been performed with satisfactory results.

In a preliminary experiment a sample of leucite, taken without regard to purity, was heated with ammonium chloride to 350° in a sealed tube. Potassium chloride was formed corresponding to 18.06 per cent of potash, and in the leached residue 6.90 per cent of ammonia was found. The foreseen reaction had occurred, and more careful work was accordingly undertaken.

Our material consisted of a large irregular crystal of leucite from Vesuvius, which yielded about 20 grms. of the pure mineral. This was ground to a uniform sample, and a portion of it was analysed; the analysis will be given presently. The sealed tube experiments were conducted precisely as in the case of analcite, and they confirmed both the preliminary test and our anticipations. Chlorides were formed equivalent to 18.53 per cent of potash, 1.08 of soda, and 0.08 of alumina; the reaction therefore was very nearly complete. The leached residue was then analysed, and the data, compared with the analysis of the original mineral, were as follows. (See Table, next column).

Leucite, then, gives the same reaction as analcite, and

	Leucite.	Residue.
SiO ₂	55.40	60.63
Al ₂ O ₃	23.69	26.44
CaO	0.16	trace
K ₂ O	19.54	0.50
Na ₂ O	1.25	0.25
NH ₃	—	7.35
H ₂ O	0.24	5.17
	100.28	100.34

yields the same ammonium compound. A closer agreement in the composition of the latter could not reasonably be demanded. Ammonium leucite is formed in both cases, by ordinary double decomposition, in a state of approximate purity; the first silicate of ammonium, we think, which has ever been prepared. At the suggestion of Dr. F. K. Cameron an attempt was made to transform ammonium leucite into the corresponding lime salt, $CaAl_2Si_4O_{12}$, by fusion with calcium chloride. The ammonium leucite was mixed with a saturated solution of calcium chloride, which was evaporated to dryness, then heated gradually to dehydration, and finally fused. Ammonium chloride was given off and identified. Upon treating the fused mass with water, filtering, and thoroughly washing the residue, a white powder was obtained, which, after drying at 100°, was analysed. It was also examined microscopically by Mr. J. S. Diller, who found it to consist of apparently isotropic grains, showing traces of incipient crystallisation. The following analysis is contrasted with the theoretical composition of calcium leucite, from which it varies considerably:—

	Found.	Calculated.
SiO ₂	54.35	60.30
Al ₂ O ₃	26.23	25.63
CaO	17.38	14.07
K ₂ O	0.16	—
Na ₂ O	0.25	—
Cl	0.28	—
Loss on ignition ..	1.24	—
	99.89	100.00

Evidently, the desired salt was not definitely obtained, and the product appears to be a mixture. The reaction, however, tends in the right direction, and deserves further study under other conditions. Probably the water which was present in the mixture of silicate and chloride took part in the changes produced; although of this we cannot be certain. It is interesting to note that the product obtained approximates in composition to the meteoritic mineral maskelynite, which is regarded as perhaps a calcium leucite by Groth.

The question now arises whether the observed reaction with ammonium chloride is limited to a few species or is fairly general. To test this point we have made preliminary experiments upon a number of other minerals, heating in a sealed tube to 350°, with the following results:—The percentage of bases removed is calculated in each case upon the original minerals; that of the ammonia is the amount found in the leached and washed residue.

Natrolite.—17.56 per cent of soda removed, 8.29 of ammonia taken up.

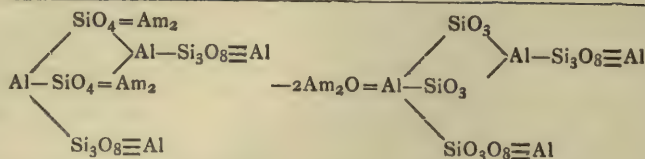
Laumontite.—4.51 of lime and 0.35 of soda removed, 3.95 of ammonia absorbed.

Stilbite.—6.54 of lime and 1.31 of soda extracted, 5.36 of ammonia in the residue.

Chabasite.—4.37 of lime and 1.13 of soda removed, 4.55 of ammonia retained.

Thomsonite.—7.94 of lime and 3.40 of soda extracted, 4.01 of ammonia taken up.

Heulandite.—4.59 of lime and 1.59 of soda extracted, 3.64 of ammonia retained.



Apophyllite.—21.59 of lime and 5.18 of potash removed, 0.79 of ammonia in residue.

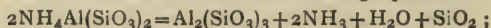
Pectolite.—20.72 of lime and 6.46 of soda extracted, 1.44 of ammonia retained.

Elæolite.—2.25 of soda taken out, 0.74 of ammonia retained.

It will at once be seen that the reaction takes place in most cases, but with varying completeness. In some instances the decomposition is very slight, in others it is near the possible limit. In each case the ammonia of the residue was obtained by decomposing the material with hydrochloric acid, supersaturating with caustic soda, distilling into tubes containing hydrochloric acid, and final weighing as ammonium chloroplatinate. Each of the minerals mentioned is to be studied more thoroughly hereafter, and prehnite, sodalite, and possibly other silicates will be added to the list.

It is evident that all of the zeolites are well suited to this new method of study, and it is more than probable that the differences in the action of ammonium chloride upon them correspond to differences in their chemical structure. But the reaction goes further than this, for it enables us to substitute in many minerals a volatile base for fixed bases, yielding silicates which split up on ignition in such a way as to shed light upon their molecular constitution.

For example, if ammonium leucite is a true metasilicate, a salt of the acid H_2SiO_3 , it should break up, when ignited, in accordance with the following equation:—



that is, one-fourth of a silica ought to be set free, measurable by extraction with sodium carbonate solution. No such splitting off occurs, however: an ammonium leucite which already contained 1.97 per cent of soluble silica gave only 1.70 per cent after ignition; hence no additional silica had been liberated. We may conclude therefore that analcite and leucite are not true metasilicates but pseudo compounds; either salts of a polymeric meta-silicic acid or mixtures of ortho- and tri-silicates as suggested in our former paper. The ammonium salt corresponding to such a mixture, when ignited, might be expected to give the accompanying reaction (see above)—a reaction which is in harmony with our experimental results. In it no free silica appears; and many, if not all, conditions of the problem are satisfied. Other formulæ, however, are possible; so that these offer merely one explanation of the phenomena, which one may or may not be the best.

Action of Low Temperatures on some Cyclic Compounds.—V. Markovnikov.—The author has tried the effect of low temperatures for purifying the naphthenes extracted from Russian petroleum and the derivatives of these bodies, by means of crystallisation. Hexanaphthene (boiling at 80–82°) crystallises at about –46°; after three crystallisations it solidifies at –11°, as a white mass apparently formed of leaf-like crystals very different to those of benzene. The ketone, $\text{C}_6\text{H}_{10}\text{O}$, crystallises at –45°; the corresponding alcohol at the ordinary temperature; nitrohexanaphthene at –34°. Heptanaphthene, metaoctonaphthene, pentamethylene, and methylpentamethylene do not solidify at –79°, but certain of their derivatives crystallise in solid CO_2 . This method enables us to detect traces of impurities which have escaped notice during analysis.—*Journ. Soc. Phys. Chim. R.*, xxxi., p. 356.

NOTICES OF BOOKS.

Optical Activity and Chemical Composition. By Dr. H. LANDOLT. Translated with the Author's permission by JOHN MCCRAE, Ph.D. London and New York: Whittaker and Co. 1899. Pp. 158.

The contents of this volume form the eighth chapter of the first volume of Graham-Otto's "Lehrbuch der Chemie," with notes and additions thereto by the translator.

Optical activity is the power possessed by a number of bodies of being able to rotate the plane of polarisation of a plane-polarised ray of light, which is passed through them; there are two types of optical activity called *crystal* rotation, and *liquid* or *molecular* rotation.

In 1848 Pasteur made his well known discovery of the right and left-handed rotation of the crystallised sodium ammonium salt prepared from racemic acid. The crystals which cause this double rotation are said to be *enantiomorphic*. By these and other observations Pasteur introduced into science a new conception, that of molecular asymmetry; the van't Hoff and Le Bel theories, which have grown out of Pasteur's original ideas, have been brilliantly confirmed by later experience. The second part of the book deals with this subject in a very clear and succinct manner, showing the connection between the rotatory power and the chemical composition of carbon compounds, while the third part deals with the degree of rotation and chemical constitution. There is on page xi. an addendum to pp. 121–131, which should not be overlooked.

An Introduction to Analytical Chemistry. By G. G. HENDERSON, D.Sc., M.A., F.I.C., and M. A. PARKER, B.Sc. London, Glasgow, and Dublin: Blackie and Son, Limited. 1899. Pp. 228.

This introduction to analytical chemistry will be found useful by students working under a demonstrator, who will first put them through a series of simple chemical experiments illustrative of chemical theory, such as the preparation of gases, the determination of densities, &c., before beginning the course of regular quantitative analysis; some such general knowledge of the subject being essential to a proper comprehension of group analysis, which is then fully described and illustrated.

Exercises in Practical Physics for Schools of Science. By R. A. GREGORY and A. T. SIMMONS, B.Sc. (Lond.). In two parts. London: Macmillan and Co., Limited. 1899. Pp. 374.

THE advantages claimed by the authors of this work are the number and variety of the exercises used to exemplify each of the principles dealt with; the limitation of the text to instructions necessary for the performance of the experiments and for understanding the meaning of the results; the number of new and simple experimental devices it has been found possible to make use of, and the numerous illustrations which show at a glance the apparatus required and the method of procedure. The authors by no means claim too much, as we find the exercises and experiments are very well chosen, the descriptive portions of the book is clear and precise, while the illustrations though numerous are good, and will

materially help the student to follow the instructions given.

Lexicon of the Carbon Compounds. (Lexikon der Kohlenstoff-Verbindungen). By M. RICHTER. In thirty-nine parts. Hamburg and Leipzig: Leopold Voss. London and Edinburgh: Williams and Norgate. 1899. Parts 13 to 39. Pp. 2482.

THE first twelve parts of this excellent work have already been noticed in our columns (vol. lxxx., p. 229), the remaining parts, making thirty-nine in all, have now been published, and show that the author's forecast of about 65,000 carbon compounds, has been considerably exceeded, no fewer than 74,174 being now registered, so continuous and increasing are the fresh discoveries constantly being made in this far-reaching subject.

The two volumes now completed form a monument of patience and industry, and must be of immense value to scientific chemical research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 13, March 26, 1900.

Deviation of Radium Rays in a Magnetic Field.—Henri Becquerel.—M. and Mme. Curie have recently shown that the rays emitted by radium carry negative electric charges. The author continues the research by measuring the electrostatic deviation of the rays. This measurement is particularly interesting because it allows of the determination of the velocity of translation of the electric charges and the proportions of the material masses involved in the charges transmitted. The arrangement consists essentially in allowing a very narrow pencil of rays to pass between two little charged plates, and receiving the pencil on a photographic plate enclosed in black paper. The fine metallic wires placed in front of the sensitive plate give shadow lines, which allow of accurate measurement. It is found that the pencil emitted by radium is repelled by the negatively charged plate. By reversing the direction of the field, the displacements are reversed. The author used for his experiments two small rectangular copper plates 3.45 c.m. high. These were placed vertically and fixed, by means of paraffin, so as to leave a space, 1 c.m. thick, of air between them. In this space the electric field was measured by the difference of potential between the plates in C.G.S. units. One of the plates was to earth and the other to a battery of six large jars, whose capacity considerably reduced the velocity of the variation of potential between the two plates under the influence of radium. A Henley's electrometer in connection with the battery had been previously graduated by observation, so as to give approximately the potential of the battery. During the experiment this potential was kept constant by constantly re-charging the battery by an influence machine. The photographic plate, wrapped in black paper, was fixed outside the field, the radio-active material being placed below the field, in a little lead vessel. By this arrangement, numbers were obtained from which the author calculates the deviation of the rays.

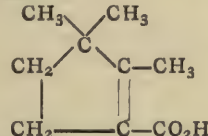
Selenide of Zinc and its Dimorphism.—M. Fonze-Diacon.—The author prepares crystallised zinc selenide (a) by the action of seleniuretted hydrogen on zinc chloride; (b) by the reduction of zinc selenate under the influence of carbon and hydrogen; and (c) by the fusion of precipitated zinc selenide in the electric furnace. He obtains hexagonal zinc selenide constituting the dimorphous form of cubic selenide prepared by M. Margottet.

By a similar method cadmium selenide can be prepared in the hexagonal system.

Hydrated Peroxides of Barium.—M. de Forcrand.—In a former communication on the hydrated barium peroxides, the author based all his calculations on a manifestly inexact assumption, owing to an error of sign: $\text{BaO} \cdot 9\text{H}_2\text{O} + \text{water} = +14.1 \text{ cal}$. He therefore repeats the experiments and calculations, and gives the corrected numbers.

New Chlor-compound of Mercury and Antipyrine.—J. Ville and Ch. Astre.—Hirsch and C. Schuyten have announced the preparation and properties of halogen mercuric derivatives of antipyrine corresponding to the general formula $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O} \cdot \text{HgR}_2$. The corresponding iodine compound is not known, in spite of many attempts to prepare it. Whilst making another attempt to realise this iodine compound, the author was led to obtain some new halogen derivatives of antipyrine corresponding to the general formula $2(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}) \cdot \text{HgR}_2 \cdot \text{HR}$; in which R represents the monovalent halogen radicle. The chlor-compound was obtained by the action of mercuric chloride on antipyrine in presence of sodium chloride and hydrochloric acid; this latter being indispensable for obtaining a crystalline product.

Constitution of Isolauroic Acid.—G. Blanc.—In a recent paper, the author confirmed his statement that the constitution of isolauroic acid ought to be represented by the formula—



contrary to the theories of W. H. Perkin, jun. The present paper establishes the above formula in a definite manner. When isolauroic acid is treated with sodium amalgam in alkaline solution, dehydro-isolauroic acid is obtained, $\text{C}_9\text{H}_{14}\text{O}_3$. This acid is a γ -ketonic acid, and not a δ -acid alcohol, as Perkin affirmed.

MISCELLANEOUS.

The Chemical Society of Paris.—It is officially announced that an international Banquet will be held by the Chemical Society of Paris in honour of those gentlemen who, by their presence at the Universal Exhibition, will represent pure and applied chemistry. The date fixed for the banquet is Thursday the 19th July, when the chair will be taken by M. Berthelot, Honorary President.

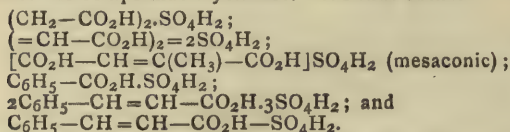
Royal Institution.—On Tuesday next, April 24th, Dr. H. R. Hill will deliver the first of a course of three lectures at the Royal Institution on "Studies in British Geography." On Thursday, April 26th, Professor Dewar will commence a course of four lectures on "A Century of Chemistry in the Royal Institution." On Saturday, April 28th, Professor Stanley Lane-Poole will deliver the first of two lectures on "Egypt in the Middle Ages." The Friday Evening Discourse on April 27th will be delivered by Lord Kelvin, the subject is "Nineteenth Century Clouds over the Dynamical Theory of Heat and Light." The discourse on May 4th is on "Pottery and Plumbism," and the lecturer will be Professor T. E. Thorpe.

The Nitrification of Organic Nitrogen.—V. Omeliansky.—According to the experiments made by the author, pure cultures of the nitrifying bacteria have no action on the nitrogen of organic compounds. Contrary to what has been alleged, this negative result is not due to too great a concentration. The oxidation of the organic nitrogen requires that this element should be first transformed into ammonia by the co-operation of an organism

capable at least of effecting the ammoniacal fermentation of the organic compounds. The opposite conclusions formulated by Frankland, Warington, and Stutzer are, according to the author, based on errors of observation. The author confirms his negative conclusions by a very complete series of synthetic experiments. He took pure cultures of *B. racemosus*, of *B. nitrosomonas*, and of *B. nitrobacter*, and cultivated them together in ordinary alkaline broth. With *B. racemosus* + *nitrosomonas* + *nitrobacter*, the nitrification is accomplished right up to nitric acid, passing through ammonia and nitrous acid. With *B. racemosus* + *nitrosomonas*, the action stops at nitrous acid. With *B. racemosus* + *nitrobacter* only ammonia is formed, since the absence of organisms giving rise to nitrous acid suppresses the alimentionation of the nitrifying organism. Finally, with *B. nitrosomonas* + *nitrobacter* no action whatever was observed, even after the lapse of six months.—*Centralbl. f. Bakter.*, 1899, p. 473.

Transformation of Trimethylene into Propylene.—S. Tanatar.—The author has observed that by very rapidly passing a mixture of trimethylene and propylene into cold bromine, the second is totally absorbed, while the first is recovered almost integrally; in the same way we can, by submitting trimethylene to the successive and repeated action of bromine with heat, completely transform it into bromide of propylene. Trimethylene being soluble in sulphuric acid, the author prefers the bromine method for demonstrating the transformation of trimethylene into propylene under the influence of heat. He uses a single bromine wash bulb, placed in the dark, followed by a soda wash-bulb; the speed of the current was 6 litres per hour. Under these conditions, after four hours, while operating on 7.5 litres of purified trimethylene with bromine, and avoiding all loss due to solubility, almost the theoretical quantity of bromide of propylene boiling at $141-143^{\circ}$, was obtained. A comparative test, made with pure trimethylene, showed that this latter is not absorbed by bromine to an appreciable extent except at 20° in sunlight; the products of the reaction consist essentially of bromide of trimethylene boiling at $155-156^{\circ}$, and small quantities of the products above and below.—*Berichte*, xxxii., p. 1965.

Combinations of some Organic Acids with Sulphuric Acid.—S. Hodgewerff and W. A. van Dorp.—Certain acids dissolve in sulphuric acid (at 96 per cent H_2SO_4), giving compounds of addition; on being cooled in ice the compounds crystallise. We thus obtain—



These bodies are very unstable, and are decomposed by all liquids.—*Revue Trav. Ch. P.-B.*, xviii., p. 211.

Obstacle opposed to Chemical Reactions by the Positions of Certain Groups.—C. Paal and F. Härtel.—Following up their previous research, the authors have now been occupied with the examination of the *o*-oxybenzylised bases; one of the authors, with M. Benker, has already shown that *p*-nitrobenzyl-*o*-nitroaniline, as well as *o*-nitrobenzyl-*o*-nitraniline, were not able to furnish acetylated derivatives, while the corresponding *m*- and *p*-derivatives gave them easily. It was found advisable to repeat the experiments with the *o*-oxybenzylised bases, and with this end in view the authors have prepared the three *o*-oxybenzyl-nitranilines. Experiments made with these bases have shown that the *o*-oxybenzyl-*m*- and *p*-nitranilines may be acetylated either in the hydroxyl group or in the iminic residue, while in *o*-oxybenzyl-*o*-nitraniline the acetyl group only enters the hydroxyl. With regard to the colour of the compounds, it has been remarked that *o*-oxybenzyl-*o*-nitraniline, which is red, gives a yellow acetyl derivative, while the mono- and the di-substituted products of *m*- and *p*-nitranilides are colourless. The introduction of the acetyl

residue into the phenolic hydroxyl apart from the chromophore "nitro" group only weakens the shade, while the substitution in the iminic residue, joined to the same nucleus as the nitro group, completely neutralises it. The bases examined have been prepared by the condensation of *o*-oxybenzyl alcohol (saligenine) with the three nitranilines; they behave generally, from the point of view of acetylation, in the same way as the nitrobenzylised nitranilines. Full details of their preparation and properties are given in the paper.—*Berichte*, xxxii., p. 2057.

MEETINGS FOR THE WEEK.

- TUESDAY, 24th.**—Royal Institution, 3. "Studies in British Geography," by Hugh Robert Mill, D.Sc., LL.D., &c.
WEDNESDAY, 25th.—Institution of Mining and Metallurgy, 8. "The Electrical Precipitation of Gold on Amalgamated Copper Plates," by Dr. T. Kirke Rose. "Notes on the Namaqualand Copper District," by J. A. Chalmers. "A Note on Hand Concentration Tests," by Walter McDermott. "Notes on the Elmore Concentrating Process," by C. M. Rolker.
THURSDAY, 26th.—Royal Institution, 3. "A Century of Chemistry in the Royal Institution," by Prof. Dewar, M.A., LL.D., F.R.S.
FRIDAY, 27th.—Royal Institution, 9. "Nineteenth Century Clouds over the Dynamical Theory of Heat and Light," by Lord Kelvin, G.C.V.O., D.C.L., LL.D., F.R.S.
Physical, 8. (In the Solar Physics Observatory, Exhibition Road, South Kensington). "A Short Account of the Physical Problems now being Investigated at the Solar Physics Observatory, and their Astronomical Applications," by Sir Norman Lockyer. Weather permitting, the 36-inch, 10-inch, and 9-inch telescopes will be used for the observation and photography of celestial objects and their spectra. The Apps-Spottiswood coil and 21-ft. Rowland grating will also be in operation.
SATURDAY, 28th.—Royal Institution, 3. "Egypt in the Middle Ages," by Prof. Stanley Lane-Poole, M.A.

ROYAL INSTITUTION OF GREAT BRITAIN, ALBEMARLE STREET, PICCADILLY, W.

Professor DEWAR, M.A., LL.D., F.R.S.,

M.R.I., Fullerian Professor of Chemistry, R.I., will, on THURSDAY next, APRIL 26th, at THREE o'clock, begin a course of Four Lectures on "A CENTURY OF CHEMISTRY IN THE ROYAL INSTITUTION."

Subscription to the Course, Half a Guinea. To all the Courses in the Season, Two Guineas.

Tickets may be had at the Office of the Institution.

THE LONDON HOSPITAL MEDICAL COLLEGE.

The SUMMER SESSION COMMENCES on MAY 1.

The Hospital is the largest in the Kingdom; nearly 800 beds are in constant use, and no beds are closed. Being the only general hospital for East London—i.e., for a million and a half people—the practice is immense. In-patients last year, 11,622; out-patients, 178,838; accidents, 17,370; major operations, 2320.

APPOINTMENTS.—Owing to the enormous number of patients, more appointments are open to Students than at any other hospital. Sixty qualified appointments are made annually, and more than 150 Dressers, Clinical Clerks, &c., appointed every three months. All are free to Students of the College. Holders of resident appointments have free board.

SCHOLARSHIPS AND PRIZES.—Twenty-seven Scholarships and Prizes are given annually. Students entering in May can compete for five Entrance Scholarships in September.

Special arrangements have been made to enable Students entering in May to present themselves for examination in Chemistry, &c., in July.

SPECIAL CLASSES are held for the University of London and other higher Examinations. Special entries for Medical and Surgical Practice can be made. Qualified practitioners will find excellent opportunities for studying the rarest diseases.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2109.

ON THE WEIGHT OF HYDROGEN DESICCATED BY LIQUID AIR.*

By Lord RAYLEIGH, F.R.S.

IN recent experiments by myself and by others upon the density of hydrogen, the gas has always been dried by means of phosphoric anhydride; and a doubt may remain whether, on the one hand, the removal of aqueous vapour is sufficiently complete, and, on the other, whether some new impurity may not be introduced. I thought that it would be interesting to weigh hydrogen dried in an entirely different manner, and this I have recently been able to effect with the aid of liquid air, acting as a cooling agent, supplied by the kindness of Professor Dewar from the Royal Institution. The operations of filling and weighing were carried out in the country as hitherto. I ought, perhaps, to explain that the object was not so much to make a new determination of the highest possible accuracy, as to test whether any serious error could be involved in the use of phosphoric anhydride, such as might explain the departure of the ratio of densities of oxygen and hydrogen from that of 16 : 1. I may say at once that the result was negative.

Each supply consisted of about 6 litres of the liquid, contained in two large vacuum-jacketted vessels of Professor Dewar's design, and it sufficed for two fillings with hydrogen at an interval of two days. The intermediate day was devoted to a weighing of the globe empty. There were four fillings in all, but one proved to be abortive owing to a discrepancy in the weights when the globe was empty, before and after the filling. The gas was exposed to the action of the liquid air during its passage in a slow stream of about half a litre per hour through a tube of thin glass.

I have said that the result was negative. In point of fact the actual weights found were 1/10 to 2/10 m. grms. heavier than in the case of hydrogen dried by phosphoric anhydride. But I doubt whether the small excess is of any significance. It seems improbable that it could have been due to residual vapour, and it is perhaps not outside the error of experiment, considering that the apparatus was not in the best condition.

NOTE ON THE DETERMINATION OF MANGANESE AS SULPHIDE.

By J. and H. S. PATTINSON.

IN determining the amount of manganese in manganese ores, &c., by the sulphide method care should always be taken to treat the filtrates from the sulphide of manganese precipitates so as to obtain the manganese which they may still hold in solution. We find that when all the precautions to secure the complete precipitation of the manganese from its solutions by sulphide of ammonium described in Fresenius's "Quantitative Analysis" have been carefully observed, the filtrates still invariably contain some manganese in solution, and sometimes a notable quantity. This can be ascertained and the amount determined by acidifying the filtrate, oxidising precipitated sulphur by bromine, and then adding excess

of ammonia and bromine to precipitate the manganese as oxide. The manganese thus obtained should, of course, be added to the principal sulphide precipitate.

The final precipitate of sulphide of manganese should also always be examined as to its purity, for we find that it very often contains small quantities of barium, cobalt, iron, silica, &c., sufficient to materially affect the result even although the solution of the manganese ore has been specially treated to eliminate these constituents before the sulphide of ammonium is added. In ores containing much lime or magnesia the sulphide precipitate may also contain these substances.

If the precautions above mentioned are not attended to, the correct amount of manganese contained in an ore will not be obtained by the analyst, unless, by chance, the errors of deficiency and excess should exactly neutralise each other.

ON THE SEPARATION OF NICKEL AND IRON WITH AMMONIA

By FRED IBBOTSON and HARRY BREARLEY.

A GOOD illustration of the difference of opinion which may be held of a simple analytical process is afforded by the separation of iron and nickel by means of ammonia. To "precipitate with ammonia, filter off the iron, &c.," appears to be such a matter as one could not get wrong about. Amongst the published and private opinions we have gathered, however, are all kinds ranging from "absolutely worthless" to "thoroughly trustworthy." In operating under varying conditions we have realised these extreme opinions, and arrived at a fairly simple explanation of the differences.

By pouring an excess of ammonia into an aqua regia solution of 1 grm. of a 10 per cent FeNi alloy, or by pouring the alloy solution into the ammonia, the Ni in the filtrate would vary from 3 to 30 per cent of the correct amount, according to the excess of ammonia used; these results justify the expression "absolutely worthless."

A number of imperfect separations are popularly explained by supposing that at the moment a precipitate is formed it exerts some peculiar influence on the element which should remain in solution, and partly "carries it down;" but in this case, if the iron seized on the nickel at the moment it becomes precipitated as $\text{Fe}_2(\text{HO})_6$, we might properly expect to find that after careful neutralisation, i.e., formation of $x\text{Fe}_2\text{Cl}_6y\text{Fe}_2(\text{HO})_6$, the nickel carried down would be less, because the ferric chloride remaining to be decomposed is less. There is no foundation for such theorising; such a modification does not at all improve the separation.

If we precipitate a solution of ferric chloride with an excess of ammonia, add a faintly acid or ammoniacal solution of nickel chloride, shake and filter, we find almost as little nickel in the filtrate as though the nickel had been present when the iron was precipitated; this shows that the act of forming $\text{Fe}_2(\text{HO})_6$ has nothing to do with the imperfect separation. The error arises through the absorption of the ammoniacal nickel solution by the ferric hydrate, just as sand, filter-paper, &c., will extract particular salts from their solutions, or from mixtures of salt solutions.

Whatever modifies the precipitated ferric hydrate or the ammoniacal nickel solution may modify the separation. To this end we have precipitated with ammonia in the presence of such acids as would form basic salts with the iron, such as phosphates, chromates, molybdates, &c.; the separations were mostly worse with than without this modification.

The most promising modifications have to do with the ammoniacal nickel solution; this is recognised, with more or less reason, by the practice of adding salts of ammonia before precipitating the iron. The value of adding such salts was illustrated by neutralising 50 c.c. ammonia

* Read before the Royal Society, April 5, 1900.

(0.880) to $(\text{NH}_4)\text{Cl}$, $(\text{NH}_4)\text{NO}_3$, and $(\text{NH}_4)_2\text{SO}_4$ respectively, adding a solution containing 1 grm. of iron and 0.1 grm. of nickel, and precipitating at boiling point with the same amount of ammonia in each case; the amounts of nickel remaining in solution are shown in the table:—

Ammonia salt.	Grm. Ni recovered.
Chloride	0.0607
Nitrate	0.0584
Sulphate	0.0573
None	0.0083

By keeping all else constant the results are better as the ammonia salt is increased or as the excess of ammonia is increased, so that by using about 100 grms. of ammonium chloride and about 50 c.c. strong ammonia in excess we may obtain a "thoroughly trustworthy" separation. The following results were obtained by using large amounts of ammonium sulphate and ammonia, the amount of iron in each case being 1 grm.:—

Ni added.	Ni found.
0.01	0.0098
0.02	0.0197
0.03	0.0300
0.05	0.0497
1.00	0.9980

In order to effect an accurate separation by the use of ammonia salts, much larger amounts must be added than are needed to form the respective chloride, nitrate, or sulphate of nickel ammonia. Except economically there is no disadvantage in this so long as the subsequent estimation of the nickel is not interfered with; by substituting potassium cyanide, however, a perfect separation can be effected when very little more KCN is present than is needed to form $\text{Ni}(\text{CN})_2 \cdot 2\text{KCN}$. Thus, the decigram. of nickel mixed with 1 grm. of iron required 66.4 c.c. KCN; with the varying amounts of KCN shown below the nickel which remained in solution when the mixture is poured into an excess of ammonia is as indicated.

C.c. KCN used.	Grm. Ni recovered.
70	0.09991
100	0.09985
150	0.09994

In the above series the nickel was estimated cyanometrically after boiling the acidified solution so as to decompose the double cyanide and drive out the HCN. The cyanide is not, we are informed, a convenient solution from which to precipitate nickel electrostatically, but such as are wedded to gravimetric processes will find that after precipitating the iron with caustic soda instead of ammonia the cyanides are readily decomposed, and the Ni_2O_3 precipitated with bromine (and soda if necessary).

If a standard solution of potassium cyanide be used in this last described process it is quite feasible to estimate the excess of KCN in an aliquot part of the filtrate, by means of silver nitrate and potassium iodide, and so calculate the amount of nickel present in the alloy. This is the most rapid process we know of estimating nickel in ferro-alloys which includes also a separation of the iron; we have used it with satisfaction for some years. With care to dissolve always in the same amount of acid the operations may be concluded in the same time as is taken to make an Eggertz carbon test on the stage of a Siemens furnace, and as it is not interfered with by the presence of chromium it is well suited to the circumstances under which such tests are required, *i.e.*, in the manufacture of ordnance. An outline of the process is: Add ammonia to the acid solution of the sample until at least all the free acid is neutralised, add an excess of standard KCN, pour into an excess of ammonia, and titrate a portion of the filtrate with AgNO_3 in the well-known manner. Such an excess of ammonia as makes the filtrate not too alkaline for the subsequent titration is ample; the excess of KCN should not be needlessly large. Some examples are:—

Per cent Ni present.	Per cent Ni found.
5.0	5.03
3.0	3.00
1.0	1.02
35.0	35.07
73.5	73.5

In nearly every case the steel-works analyst, to whom these rapid methods chiefly appeal, knows to 1 per cent or so how much nickel is present in the materials being examined, and the excess of KCN can be added accordingly, but where the percentage may be 5 or 50 the process is less suited because the excess of KCN adheres to, or combines to, a slight extent with the precipitated iron, and when the excesses are very large this error becomes appreciable. As an example, we quote a 3 per cent nickel steel which was purposely treated with varying excesses of KCN:—

Percentage excess of KCN.	Per cent Ni found.
5	3.00
25	3.03
50	3.04
150	3.15

Nickel is absorbed by precipitated ferric hydrate to an appreciable extent from ammoniacal solutions only; in fact, the nickel thus removed from solution is largely re-dissolved on making the solution so slightly acid that the $\text{Fe}_2(\text{HO})_6$ is hardly at all dissolved, and separations have been based on this fact. With like reason, when the iron is precipitated in the presence of ammonium chloride with so little ammonia that finally the filtrate is distinctly acid, the separation is a good one. The Schwarzenberg separation is but a particular mode of performing this operation; it depends on the nice adjustment, in the cold solution, of the $x\text{Fe}_2\text{Cl}_6 \cdot y\text{Fe}_2(\text{HO})_6$ compound, so that when the ammonia is no longer to be added, to use Fresenius's words, "the fluid fails to recover its clearness after standing some time in the cold, but, on the contrary, becomes rather more turbid than otherwise."

Perhaps the least troublesome way of making this separation is to heat the acid solution of iron and nickel to boiling-point. At this temperature the ferric hydrate first precipitated is easily dissolved by the undecomposed ferric chloride, and very little time is lost in obtaining a turbid solution, which, however, does not hold any real filtrable precipitate, and is really obtained with less ammonia or ammonium carbonate than would be needed to form a lasting precipitate in the cold solution. From this point, only a very dilute solution of ammonia should be used, and when the total ammonia added is equal to, or somewhat less in amount than would be needed to form a permanent turbidity if the neutralisation had been made in the cold solution, the iron will have been precipitated.

The operation requires considerable care and attention, but is not otherwise a difficult one; its success depends on keeping the solution acid throughout. If the solution be ever so slightly alkaline, the separation is not nearly perfect. Appended are examples of separations made as above, but omitting the addition of ammonium chloride (II.); in the same way, but adding 2 or 3 c.c. acetic acid after precipitating (I. and V.); as in II., but adding a few c.c. acetic acid before precipitating (III. and IV.). The process could be modified in various other ways without affecting the accuracy of the separation.

	Present.		Nickel found.
	Fe. Grms.	Ni. Grm.	
I.	1	0.20	0.1999
II.	1	0.10	0.0998
III.	1	0.05	0.0497
IV.	2	0.10	0.1002
V.	2	0.03	0.0298

Technical Department,
University College, Sheffield.

NEW METHOD FOR THE ESTIMATION OF PHOSPHORIC ACID IN PHOSPHATES.

By W. HOFFMEISTER.

THE author has given up the use of citric acid as a solvent for phosphoric acid in bone ashes, and all phosphates in general, with the exception of Thomas's scoria. He proposes the use of an ammoniacal solution of humic acid in which the phosphate is suspended and carefully stirred, at the same time passing a current of carbonic acid through the liquid.

Into a 2 litre flask, in which a little sand has been placed, is poured a solution of 15 grms. of humic acid in dilute ammonia, 5 grms. of the phosphate under examination, and at least 1 litre of water. A current of carbonic acid is passed through the liquid for twelve hours, adding a little ammonia from time to time. The liquid is then poured into another flask, the sand is washed, and the wash-waters added to the original liquid; the whole is then made up to a known volume, and filtered. Four-fifths of the volume are then taken and evaporated to dryness on the water-bath with a little hydrochloric acid, the residue is taken up with water and hydrochloric acid, filtered, washed, and the clear solution then made up to 100 c.c. In a known volume of this solution the phosphoric acid, the iron, and the lime are estimated, and the silica in the residue.—*Landw. Versuchstat.*, 1, p. 363.

THE COMMERCIAL SEPARATION OF PLATINUM FROM GOLD.

By E. PRIWOZNIK.

SCRAPS, filings, &c., of gold containing platinum are put on one side in minting operations, as the ordinary methods of gold refining cannot be applied to them with success. The following method has been successfully used by the author when dealing with large quantities of such scrap.

The sifted filings are digested with nitric acid of 1.199 density, until no more silver is dissolved. During this operation a small quantity of platinum also goes into solution in the form of platino-nitrite of silver. The metallic residue is washed and exhausted with aqua regia of the following composition:—

Concentrated hydrochloric acid	100 volumes
Water	43 ..
Water	143 ..

When the chloride of silver which deposits on the surface of the metal stops all further action, the solution of chloride of gold is decanted, and the chloride of silver removed by washing the metal with a little ammonia. The metal may then be treated a second time with aqua regia.

After six successive treatments with aqua regia and ammonia, the metallic residue consists of pure platinum. The acid solution which contains the gold is evaporated down with an excess of hydrochloric acid, to drive off the nitric acid, until the chloride of gold crystallises. The chloride of gold is re-dissolved, and the small quantity of platinum present is precipitated by means of chloride of ammonium. Finally, the gold is precipitated by ferrous sulphate.

The filings treated by the author contained:—

Gold	28.05 per cent
Silver	10.56 ..
Platinum	45.46 ..
Copper	15.93 ..

If the metals form a true alloy it is preferable to previously melt this alloy with 3 parts of lead, or, what is even better, 3 parts of zinc. The metal is then granulated

and treated with sulphuric acid, which dissolves the zinc, and the spongy residue is treated in the manner above described.—*Österr. Zeits. f. Berg. u. Hüttenwesen*, 1899, p. 356.

ALINITE.

THE preparation known under the name of *alinite* is a yellowish powder containing a pure culture of Caron's *Bacillus Ellenbachensis alpha*. This bacillus has the property of assimilating atmospheric nitrogen, and thus renders the use of nitrated manures for the culture of cereals more or less superfluous.

Stoklasa has shown that this bacillus is a denitrifying one and that it decomposes fibrine, making 22 per cent of its nitrogen soluble after seventy-six days; while in another experiment, without inoculation, only four per cent of the nitrogen passed to the soluble state. Analogous experiments with peat show that in seventy-two days 42 per cent of the nitrogen passed into the soluble state under the influence of this microbe. Finally, experiments made with barley showed that fixation of free nitrogen took place in the presence of alinite.

Stoklasa, however, came to the conclusion that the principal work of the bacillus consisted in the transformation of the nitrogen of the organic matter in the soil into assimilable nitrogen.

Stutzer and Hartleb concluded that the bacillus is aerobic, that is to say, very similar to the *B. Mycoides* and the *B. Megatherium*, and that in its manner of behaviour with nitrated substances it resembles the bacteria of putrefaction.

According to Lauck, alinite would be a pure culture of the *Bacillus subtilis Ehrenberg* developed in a special preparation of powdered potato. He found that this bacillus has the property of liquefying the albumen of a boiled egg. A culture of this bacillus, to which was added some peptone, soon gave off the characteristic smell of trimethylamine.

As for the practical utility of alinite, Caron states that according to his experiments the use of this substance increases the crops. On the other hand, Moercker shows it to be absolutely inefficient.

A large number of experiments have been carried out in the open field, but the results have been very contradictory.—*Biedermann's Centralblatt*, 1899, xxviii., 156.

THE PRODUCTION OF CRYSTALLISED SALTS OF BISMUTH.

By A. DE SCHULTEN.

PART I.

OXYCHLORIDE of bismuth, BiOCl, has been obtained crystallised in white flakes having a micaceous lustre, by Jacquelin, by passing a current of steam through chloride of bismuth kept in fusion (*Ann. Chim. Phys.*, lxvi., p. 113). I have prepared crystals of this substance by the following process:—

Three grms. of oxide of bismuth are dissolved in 300 c.c. of hydrochloric acid of 1.05 density, after heating to boiling; 2.5 litres of boiling water are added, and the whole filtered; the filtrate is heated until the whole of the precipitate is re-dissolved, and then allowed to cool. After standing for 24 hours crystals of oxychloride of bismuth are formed; these are washed with water acidulated with hydrochloric acid, then with pure water. The analysis of the crystals gives the following figures:—

	Found.	Calculated for BiOCl.
Bi	80.38	80.21
Cl	13.61	13.64
O	6.01 (by diff.)	6.15
	100.00	100.00

When heated to bright redness these crystals melt, forming a crystalline glass, and give off fumes of chloride of bismuth.

Oxychloride of bismuth occurs as clear, colourless, quadratic crystals. The facets β (001) and $\beta\frac{1}{2}$ (111) are observed. The crystals are uniaxial and negative; their density is 7.717 at 15°; their molecular volume is thus 33.7.

Oxybromide of bismuth, BiOBr, is obtained in the crystalline state in the following manner. We dissolve 3 grms. of oxide of bismuth in 50 c.c. of hydrobromic acid of 1.38 density; heat the solution to boiling, add 1500 to 1600 c.c. of boiling water, and heat until the whole of the precipitate is re-dissolved. On cooling the solution, a small quantity of well crystallised oxybromide of bismuth is formed. The crystals are washed with water, acidulated with hydrobromic acid, and then with pure water. The analysis of the crystals gives the following figures:—

	Found.	Calculated for BiOBr.
Bi	68.43	68.48
Br	26.24	26.26
O	5.33 (by diff.)	5.26
	100.00	100.00

When heated to bright redness, these crystals melt, forming a crystalline glass, and give off fumes of bromide of bismuth.

Oxybromide of bismuth* occurs as clear, colourless, quadratic crystals. The same facts are observed as with the oxychloride. The crystals are uniaxial and negative. Their density is 8.082 at 15°; their molecular volume is therefore 37.7.

Oxyiodide of bismuth, BiOI, is obtained in the crystalline state in the following manner: 0.250 gm. of oxide of bismuth is dissolved in 40 c.c. of hydriodic acid of 1.2 density, the solution is diluted with 6 litres of cold water, and the whole heated on the water-bath. As the temperature rises beautiful crystals of oxyiodide of bismuth are formed. These crystals are washed with pure water. In the preparation of oxyiodide of bismuth it is indispensable to use a large excess of hydriodic acid to prevent the formation of black crystals of iodide of bismuth by the ulterior action of the water. The analysis of the crystals gives the following results:—

	Found.	Calculated for BiOI.
Bi	59.44	59.34
I	35.76	36.11
O	4.80 (by diff.)	4.55
	100.00	100.00

When heated to redness these crystals melt with decomposition.

Oxyiodide of bismuth occurs as clear, quadratic crystals having a beautiful copper colour. Their facets are the same as those observed with the corresponding chlorised compound. The crystals are uniaxial and negative. Their density is 7.922, and their molecular volume is therefore 44.4—*Bull. Soc. Chim.*, Series 3, xxiii., No. 5.

ON THE PRESENT ASPECT OF THE QUESTION OF THE RETROGRESSION OF THE SOLUBLE PHOSPHORIC ACID IN SUPERPHOSPHATES.

By L. SCHUCHT.

SINCE the use of mineral phosphates in the manufacture of superphosphates, we find ourselves in the presence of questions which had not previously existed in the case of bone and guano phosphates. There was then no motive or considering the question of the retrogression of the

soluble phosphoric acid, owing to the absence of the body which caused this reaction. Such phenomena only began to be evident when we became forced to have recourse to mineral phosphates. These phosphates were submitted to the same treatment as those previously used, and it was found before long that the phosphoric acid which had been rendered soluble retrograded, or, in other words, it gradually became insoluble. When once this fault was recognised, efforts were made to find a remedy, and the method of breaking up the mineral phosphates has been modified and improved to such a degree that at the present time superphosphates can be obtained which are in no way inferior to those prepared from pure raw materials.

But it may be asked, what are the bodies which cause the phenomena of retrogressions? Although this question may not yet be quite decided, we know at least what precautions to take when employing any particular class of raw phosphate. It is therefore necessary, before breaking up the raw phosphate, to submit a properly selected sample to a complete qualitative and quantitative analysis. The results obtained enable us to combine the bases with the acids found, to form salts, and thus to calculate the quantity of acid necessary for its decomposition. Once in possession of these facts, it is easy to make a series of disaggregation tests, using a quantity of sulphuric acid slightly higher than the theoretical amount. From these tests we can also find the amount of phosphoric acid which it is possible to make soluble, and also the degree of decomposition of the phosphate under examination.

The yield of a phosphate depends essentially upon its degree of decomposition by sulphuric acid and the nature and amount of foreign bodies it may contain,—in other words, it is necessary to know the proportion of phosphate that escapes decomposition, the nature of the insoluble residue, and the composition of the salts formed. The superphosphates are variable mixtures of salts, acids, and insoluble bodies, which, being able to react one on the other, may give rise to precipitates. We will return to this point later on, and we wish particularly to point out under what conditions a well-prepared superphosphate may undergo retrogression.

Superphosphate kept in a warehouse exists at first in the pulverulent state, without the particles being in intimate contact; but as fresh quantities are added the pile increases in height, and slowly becomes more and more solid, eventually forming a single, more or less homogeneous lump. It is only from this point that the phenomenon of retrogression is made manifest.

The hygroscopic water and the free acid are set at liberty, and complete the intimate contact of the particles till then isolated. The different bodies become, as it were, suspended in a liquid, and from that moment all the requisite conditions exist for them to act one on the other; *corpora non agunt nisi soluta*.

It is evident that in drying the superphosphate at 100° we only accelerate the decomposition, and start reactions going which, with an undried superphosphate, only take place after some time.

Florida phosphate contains about 46 per cent of soluble material— $\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$, H_3PO_4 , $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; and about 54 per cent of insoluble matter—undecomposed phosphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaH_2 , SiO_2 , H_2SiO_3 , $\text{Al}_2(\text{SiO}_3)_3$.

What is the relation between the insoluble residue and the soluble materials? The gypsum, which is the skeleton of the superphosphate, is a neutral body; it is not attacked by phosphoric acid, and Berthollet's law does not apply in this case.

Of all the above-mentioned soluble bodies, the free phosphoric acid (H_3PO_4) is the most active, and it attracts, so to speak, each of the insoluble particles to saturate its own chemical acidity. The undecomposed phosphate is attacked first, then comes the silicate, and, if this latter is present in large quantity, the phosphoric acid will not

be sufficient; there is then a loss of soluble phosphoric acid in the form of AlPO_4 and CaHPO_4 . The calcic fluoride is not attacked, and the silica does not come into the question. As for the insoluble phosphoric acid, there is no longer any left in the stored superphosphate in the form of $\text{Ca}_3\text{P}_2\text{O}_8$, but as acid phosphate of lime. With a proportion of 4 per cent of phosphoric acid in the form of H_3PO_4 , the superphosphate may contain 2 per cent of phosphoric acid as $\text{Ca}_3\text{P}_2\text{O}_8$, without there being any CaHPO_4 formed. Thus, in the warehouse, the phosphate ought to be richer in soluble phosphoric acid, but, on the other hand, the soluble phosphoric acid may form insoluble compounds.

In the second place, we must refer to the relation between the acid phosphate of lime and the salts of iron and aluminium. The ferric oxide in Florida phosphate exists in the state of FePO_4 (1 per cent), and immediately on its disaggregation it is entirely dissolved, and, with the phosphate of lime, forms the compound $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, which is found in the superphosphate. When the ferric oxide present does not exceed 1 per cent, the ferric sulphate remains in solution with the acid phosphate of lime without there being any loss of soluble phosphoric acid; but if the quantity present is greater, we must expect a retrogression of the soluble phosphoric acid, from the moment when the free phosphoric acid alone is not sufficient to stop the formation of FePO_4 . All the old ideas as to the composition of the precipitated ferric phosphate, $\text{Fe}_2\text{O}_3(\text{PO}_5)_2$, $2\text{Fe}_2\text{O}_3(\text{P}_2\text{O}_5)_3$, &c., are erroneous; there is simply $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ or FePO_4 formed.

The alumina is in the form AlPO_4 in the soluble portion, and in the state of clay Al_2SiO_3 in the gangue; free alumina, Al_2O_3 , has only up to the present been found in phosphate from Somme. Phosphate of aluminium is easily decomposed, but the sulphate is not so active on the acid phosphate of lime as ferric sulphate. We may therefore say that ferric oxide is more objectionable than alumina.

The salts of magnesia, as well as the small quantities of alkaline salts which are present in superphosphates, have no influence on the retrogression of the soluble phosphoric acid.—*Die Chemische Industrie*, 1899, p. 152.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, April 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The recent excessive rainfall ended with the last day of February, and was followed by dry weather during the first fourteen days of March. The total rainfall for the month at Oxford has been 0.50 inch, distributed over seven days. The average fall is 1.50 inches, we therefore have a deficit of 1.0 inch of rain for the month; this reduces the excess for the year to 1.61 inch, equal to 29.7 per cent on the thirty years' average.

Our bacteriological examinations of 537 samples have given the results recorded in the following table; we have also examined 37 other samples, from special stand-pipes, &c., making 574 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	282
New River, filtered (mean of 110 samples) ..	8
Thames, unfiltered (mean of 27 samples) ..	1694
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 304 samples) ..	18
Ditto ditto highest	202
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	426
River Lea, from the East London Company's clear-water wells (mean of 42 samples) ..	5

The bacteriological purity of the London water supply during the last month has been very good on the whole, there being only one occasion on which one of the filters of the Thames-derived Companies gave a higher number of microbes than 200 per c.c. All the other samples examined were well filtered, the average number of microbes not exceeding 18 in the Thames-derived Companies, and being as low as 5 in the River Lea water from the East London Water Company's mains.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 29th, 1900.

Professor THORPE, F.R.S., President, in the Chair.

DR. DYER and Mr. FRISWELL were appointed scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's Address.

In beginning his Address, the PRESIDENT congratulated the meeting on the fact that the Society continues to grow and prosper; the number of its Fellows steadily increases, and their communications continue to add to its dignity and usefulness. Its financial position is no less satisfactory.

The numerical strength of the Society was as follows:—

Number of Fellows, March 29th, 1899	2230
" " since elected	118
" " reinstated by Council	4
	2352

Removed on account of non-payment of two annual subscriptions	15
Withdrawn	20
Deaths	25
	60

Number of Fellows, March 29th, 1900	2292
Foreign Members	33

The following have died:—Joshua Buchanan, Robert Wilhelm Bunsen, Kanny Lall Dey, J. B. Edwards, Sir Edward Frankland, Charles Friedel, William Harkness, John F. Hodges, John Elias Hughes, Eric H. Jackson, William Marcet, Alexander McDougall, Walter Newton, L. F. Nilson, G. H. Ogston, Robert Oxland, R. T. Plimpton, C. F. Rammelsberg, Henry Charles Reynolds, J. G. F. Richardson, W. H. Richardson, Thomas Glazebrook Rylands, Edward C. Cortis Stanford, Sidney Augustus Sworn, Andrew Taylor, William Thorp, Ferdinand Tiemann, Peter Waage, David Watson, W. Lloyd Williams.

The passing away of so eminent a member of the Society, and of one who played such a leading part in the development of chemistry, as Sir Edward Frankland is no ordinary event in the history both of Science and of the Society, and demands a special reference. The Council have accordingly determined that Sir Edward Frankland's services shall be commemorated in the manner hitherto restricted, with the special exception of the late Professor von Hofmann, to its Honorary Foreign Members; and they have requested his pupil, collaborator, and friend, Professor Armstrong, to give a Memorial Lecture on his life-work in the ensuing autumn.

The names of the deceased Foreign Members are Robert Wilhelm Bunsen, Charles Friedel, Lars Fredrik Nilson, Carl Friedrich Rammelsberg, and Peter Waage.

Bunsen, who was elected a Foreign Member during the first session of the Society, namely, as far back as February 1, 1842, and who was long the *doyen* on the list, died on August 16, 1899, in his eighty-ninth year. His friend and pupil, Sir Henry Roscoe, a past President of the Society, has undertaken, at the request of the Council, to commemorate the signal services which Professor Bunsen rendered to physical science.

Charles Friedel, Member of the Institute and Professor of Chemistry in the Sorbonne, who was elected a Foreign Member of the Society on May 18th, 1876, died on April 20th, 1899, at the age of sixty-seven. His friend and co-worker, Professor J. M. Crafts, of the Massachusetts Institute of Technology, and a Fellow of this Society, has kindly responded to the invitation of the Council to prepare a Memorial Lecture, which he hopes to be able to deliver on some evening in the latter half of June next.

Lars Fredrik Nilson, Professor of Agricultural Chemistry in the Kongl. Landbruks-Akademien, Stockholm, and formerly Professor of Analytical Chemistry in the University of Upsala, whose name is specially connected with the chemistry of the so-called rare earths, and who was elected a Foreign Member of the Society on February 2, 1888, died on May 14, 1899, in his fifty-ninth year. Professor Otto Pettersson, of the Free University of Stockholm, who was associated with Nilson in most of his work in pure chemistry, has undertaken, in compliance with the wish of the Council, to give the Society an account of the many services which his friend rendered to chemistry, and he hopes to be able to visit London for this purpose in the first week of July next.

Carl Friedrich Rammelsberg, Geh. Reg. Rath, and Emeritus Professor of Inorganic Chemistry in the University of Berlin, who was elected a Foreign Member on May 3, 1866, died on December 28, 1899, in his eighty-seventh year. Professor H. A. Miers, of Magdalen College, Oxford, and a Fellow of this Society, has kindly acceded to the wish of the Council to prepare a memorial lecture on the life-work of the veteran mineralogical chemist, which he hopes to deliver to the Society in December next.

Peter Waage, Professor of Chemistry in the University of Christiania, whose name is best known in connection with the studies on chemical affinity which he made in association with his colleague, Professor Guldberg, died on January 13th of this year. He was elected a Foreign Member of this Society on January 20th, 1898.

Since the last Anniversary, 175 communications have been made to the Society, a number greater than in any preceding year. In character, variety, and importance they compare not unfavourably with the contributions of any former period. Abstracts of all these have appeared in the *Proceedings*, and 83 have already been published in the *Transactions*. The volume of *Transactions* for 1899 contains 120 memoirs, occupying 1166 pages; in the preceding year 102 papers were published, occupying 1038 pages.

The volumes for 1899 contains 3617 abstracts of papers, published mainly in continental journals, occupying 1796 pages, arranged as follows:—

PART I.		Pages.	No. of Abstracts.
Organic Chemistry	968	1477	
PART II.			
General and Physical Chemistry		421	
Inorganic Chemistry		417	
Mineralogical Chemistry		211	
Physiological Chemistry		236	
Chemistry of Vegetable Physiology and Agriculture		244	
Analytical Chemistry		611	
	828	2140	
Total in Parts I. and II. ..	1796	3617	

The number of abstracts dealt with in 1899 is 791 more than in the preceding year. All arrears in abstracting have at length been overtaken. The Fellows may now count upon having the monthly *résumé* of contemporary chemical literature brought to their attention as quickly as it is possible to furnish it.

It will have been observed also that the Editor has succeeded in issuing the journal somewhat earlier in the month than has hitherto been thought possible.

The question of co-operation with other English-speaking Chemical Societies in the preparation of abstracts of foreign chemical literature was referred to in the last Presidential Address. But, although the matter has been considered, the committee appointed to deal with this question has not yet reported.

637 copies of the 1883—92 Index, and 317 of the 1873—82 Index were issued to Foreign Members, Institutions, and to those Fellows who, being entitled to a Free Grant of them, had made application within the prescribed period. 565 of these applications had been received, of which 43 were those of Fellows resident abroad.

The work of compilation of the Collective Index showed the necessity of indexing the annual volumes in a more systematic manner than had been done in the past. For the last four years, the work of indexing the annual volumes has been entrusted to a special staff of indexers under the direction of the Sub-Editor. This plan has worked well as regards uniformity and consistency, but unfortunately it has not been possible, by means of it, to bring out the Annual Index with that promptitude which is desirable. The Index Committee has therefore suggested to the Council the propriety of entrusting the work of indexing to one person, to be responsible, under the direction of the Editor, for the preparation and speedy publication of the work, and the Council has sanctioned the employment, on this work, of Mrs. Dougal, who is already favourably known to the Fellows for the excellent service she rendered the Society in editing the Collective Indexes of its publications since 1873.

The Fellows are aware the Society stocks a certain number of its publications, and the question of the custody and supply of back numbers has received attention. A limited number of sets of the *Memoirs* and *Proceedings* of 1841—7, of the *Quarterly Journal*, 1849—62, and of the First Series of the *Journal* from 1863 onwards are now on sale.

As regards the Library, 790 books have been borrowed, as against 727 last year; and 114 books, 397 volumes of periodicals, and 27 pamphlets have been added, as against 67 books, 285 volumes of periodicals, and 24 pamphlets in the preceding year.

The condition of the Library Catalogue has received attention, and the Council has directed a new Catalogue to be prepared according to a scheme drawn up by the Library Committee; and the work is well advanced under the direction of Mr. Steele, assisted by Miss Morfee.

Grants amounting to £192 have been made in aid of chemical investigation.

The Longstaff Medal has been awarded to Professor W. H. Perkin, F.R.S. In making the presentation, the President said:—

"Dr. PERKIN, it gives me a special pleasure to ask you, on behalf of the Chemical Society, to transmit this medal to your son, Professor W. H. Perkin, who, to our great regret, is unable to be here to receive it in person. The Longstaff Medal has been awarded to him for his researches on closed chain compounds of the trimethylene and similar series, and for his recent important syntheses of camphor derivatives.

"The Council desire on making this award to indicate how highly we regard the contributions with which he has enriched our *Transactions*. Under his stimulating influence, the chemical laboratory of the Owens College, and especially that section of it under his more immediate direction, continues, as of old, to furnish a succession of valuable memoirs to English chemical literature. We trust that this activity may long be maintained, and that our Society may continue, as in the past, to enjoy the credit and distinction of disseminating the results of the inquiries to which his fruitful ideas give rise."

During the long vacation, the building has been thoroughly cleaned and re-decorated, and certain much needed improvements in the lavatory accommodation and in the sanitary arrangements of the building have been effected.

The accommodation at the disposal of the Society is, however, a matter of growing concern. The meeting-room seats no more than 157 persons, in spite of the increased space which was gained as the results of the alterations in 1892. This is altogether incommensurate with the present numerical strength of the Society, and, as the Fellows well know, considerable inconvenience is occasionally felt owing to the impossibility of finding room for those who wish to attend the meetings. The collection of books is gradually overspreading into every room the Society possesses, and such conveniences as the officers have for the discharge of their official business, and for the custody of the official records, are greatly curtailed by the increasing inadequacy of the space at their disposal.

The Society is indebted to several of its Fellows for additions to its artistic possessions; among these is a bust of Sir Humphry Davy, presented by Dr. Debus, a copy of which in bronze, together with its pedestal, has been given by Dr. Messel; Dr. Atkinson has presented an electrotypic medallion of Wöhler, executed by Dr. Hugo Müller, and Sir Henry Roscoe has given some photographic mementoes of his association with Bunsen and the Heidelberg Laboratory.

The Society had the pleasure of congratulating, by a suitable address, Sir George Gabriel Stokes on the occasion of his jubilee as Lucasian Professor of Mathematics, and it has since received from the University of Cambridge an exemplar of the medal which was struck in commemoration of that event.

Congratulations have also been sent to Professor Emil Fischer and Professor van't Hoff on the twenty-fifth anniversaries of their doctorates, of which acknowledgments, already published in the *Proceedings*, have been received.

The remainder of the address was devoted to a review of the progress of chemical science from the beginning of the century to the date of the formation of the Society.

Sir H. Roscoe, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*.

Prof. LIVEING, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks, Prof. TILDEN, F.R.S., the Treasurer, in giving an account of the balance sheet, which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4088; by sale of Journal and advertisements, £781 15s. 6d.; and by dividends on invested capital, £444 13s. 7d. The expenses had been:—On account of the Journal, £3388 12s. 11d.; on account of the *Proceedings*, £171 14s. 7d.; on account of the preparation of a new Card Catalogue, £35 9s. 2d.; on account of the Library, £286 17s. 3d.; House expenses, including the re-decoration of the building, £543 5s. 11d.; the total expenditure being £4993 13s. 1d. Grants amounting to £192 had been made to Fellows from the Research Fund during the year.

Attention was directed to the fact that the net income of the Society for the year being £5371 18s. 5d., and the expenses £4993 13s. 1d., the surplus is only £377 8s. 4d. This is considerably less than the amount, £578, of the Composition and Admission Fees which ought to be regarded as Capital. In view of the steadily increasing cost of the Society's publications, the recurrence of the heavy charge for the Decennial Index, and the growth of the Library, economy will have to be practised to keep the finances of the Society in a healthy condition. The Treasurer appealed to authors of papers to assist in keeping down the cost of the composing and correcting the proofs of papers communicated to the Society. At the present time the average cost of corrections amounts to more than one-third the charges for putting manuscript into type. A little more care exercised by authors in preparing for the press would result in a substantial reduction in the cost of printing.

The TREASURER, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. PAGE.

Prof. ODLING, F.R.S., proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Dr. RUSSELL, F.R.S., and carried.

Prof. H. B. DIXON, F.R.S., proposed a vote of thanks to the Officers and Council.

Prof. WARINGTON, F.R.S., seconded the motion, which was unanimously adopted.

Prof. DUNSTAN, F.R.S., responded on behalf of the Council.

Prof. DEWAR, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Mr. GROVES, F.R.S., and carried.

Dr. WYNNE, F.R.S., responded.

The scrutators having presented their report to the President, he declared that the following had been duly elected:—

President—T. E. Thorpe, Ph.D., D.Sc., LL.D., For. Sec. R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, D.C.L., LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—E. Divers, M.D., D.Sc., F.R.S.; C. E. Groves, F.R.S.; G. D. Liveing, M.A., D.Sc., F.R.S.; T. Purdie, Ph.D., F.R.S.; T. Stevenson, M.D.; John M. Thomson, LL.D., F.R.S.

Secretaries—Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—William A. Tilden, D.Sc., F.R.S.

Other Members of Council—H. Brereton Baker, M.A.; F. D. Chattaway, Ph.D., D.Sc.; Frank Clowes, D.Sc.; J. Norman Collie, Ph.D., F.R.S.; A. E. Dixon, M.D.; H. J. H. Fenton, M.A., F.R.S.; W. Gowland; C. T. Heycock, M.A., F.R.S.; D. Howard; Rudolph Messel, Ph.D.; W. J. Pope; James Walker, D.Sc.

Extra Meeting, March 29th, 1900.

Professor THORPE, F.R.S., President, in the Chair.

Sir HENRY E. ROSCOE, F.R.S., Vice-President, delivered the Bunsen Memorial Lecture.

Before commencing the Lecture, Sir Henry Roscoe read the following telegram, which he had just received from Bunsen's nephew and executor, Dr. PHILIPP BUNSEN, of Marburg:—"On the occasion of the Memorial Lecture, the Bunsen family joins sincerely with the illustrious Society, and sends respectful thanks and compliments."

The death of Bunsen on August 16th, 1899, severs the last link connecting the chemists of our time with the great men of the earlier part of the century, Berzelius, Gay Lussac, Dumas, Liebig, and Wöhler, Mitscherlich, and the two Roses, as well as with the physicists Dove, Wilhelm Weber, and Magnus, all of whom he counted amongst his personal friends. Living to the ripe age of eighty-eight years, he was destined to witness the deaths as well as the scientific births of many distinguished colleagues and pupils; of Kirchhoff, Helmholtz, Kopp, and Hermann; of Strecker, Kolbe, Kekulé, Pebal, Lothar Meyer, and, finally, of Victor Meyer, his successor in the chair at Heidelberg.

Robert Wilhelm Bunsen was born on March 31st, 1811, at Göttingen, where his father was chief University Librarian, and Professor of Modern Philology. Entering the University in 1828, he studied chemistry under Stromeyer, and graduated in 1830. He then visited Paris, Berlin, and Vienna, continuing his studies, and making the acquaintance of the scientific men of those cities, returning to Göttingen, where, in 1834, he was admitted by the University as Privatdozent in Chemistry. In 1836 he succeeded Wöhler as teacher of chemistry in the Polytechnic School at Cassel, and in 1839 was appointed Professor Extraordinarius of Chemistry at Marburg, being advanced in 1842 to the post of Ordinarius. Here he remained till 1851, when he went for a short period to Breslau, and in 1852 he accepted the chair at Heidelberg, which he occupied until his retirement in 1889. In these several positions, Bunsen laboured incessantly and devotedly for fifty-six years in the furtherance of chemical science, with the result that his name will be handed down to posterity as one whose work has earned for him the very first rank amongst chemists of the nineteenth century.

Bunsen's first published paper recorded his discovery that freshly precipitated ferric hydroxide acted as a powerful antidote in cases of arsenical poisoning, but the first research in which he showed his power was the classical one on the cacodyl compounds, which was continued for no less than six years. His important investigations on the composition of the gases of German and English blast-furnaces were of the highest practical as well as theoretical importance, and led incidentally to the devising and perfecting of his well-known system of gas analysis. In 1857, he collected in a volume the whole of his gasometric researches, and of this—the only book he ever published—a second and greatly enlarged edition appeared in 1877.

The construction of his carbon-zinc battery marks an era in the economic production of electricity. He showed how it could be employed as a means of illumination; he

determined its power of doing work, and used it to prepare electrolytically many metals hitherto unknown in a coherent form, notably magnesium, the preparation of which had baffled Davy. These researches led in turn to his inventions of the well-known "grease spot" photometer and the ice- and the vapour-calorimeters. Along with the lecturer, he carried out the photochemical researches based on the action of light on a mixture of equal volumes of hydrogen and chlorine, pronounced by Ostwald to be "the classical example for all further researches in physical chemistry."

The famous researches on spectrum analysis of Kirchhoff and Bunsen gave, not only a full explanation of Fraunhofer's lines in the solar spectrum and a knowledge of the composition of the sun and the fixed stars, but led in Bunsen's hands to the discovery of two new metals, caesium and rubidium, and in the hands of others, of thallium, indium, gallium, and other elements.

In 1846, Bunsen spent three months and a half in Iceland, as a member of an expedition promoted by the Danish Government, of which the outcome was his well-known series of investigations of the volcanic and pseudo-volcanic phenomena of that island. He worked for some time at the separation of the metals in the residues left after the extraction of the platinum, as carried out in the Imperial Mint at St. Petersburg, and in his account of this is to be found a description of his filter-pump actuated by a fall of water.

To Bunsen and Schischkoff we owe the first exact examination both of the gaseous and solid products of the explosion of gunpowder. Perhaps his name is most widely known in connection with his burner for gas, devised to provide a flame both hotter and more steady than that of the argand burner with wire-gauze top previously in use. Not only as a source of heat, but also most ingeniously as an analytic agent, was the flame of his gas burner employed in producing the delicate and characteristic "flame reactions." Important also are his papers on the colour of water, iodometric methods, and water analysis.

The remainder of the Lecture consisted of the lecturer's personal recollections of Bunsen, and of the Heidelberg Laboratories from 1852 onwards, with a description of the character and methods of work of the Master as a teacher and a lecturer, and of the relations existing between him and his pupils.

Considerate and generous towards the opinions of others, he held firmly to his own, which at times he did not fail strongly to express; simple and straightforward, he disliked assumption and hated duplicity; single-minded and wholly devoted to his science, he abhorred vanity and despised popularity hunting.

At the time of his death, Bunsen had been for many years our senior Foreign Member, having been elected on February 1, 1842, during the first session of our Society. In 1858 he became a Foreign Fellow of the Royal Society, and in 1860 the Copley Medal was awarded to him. To Bunsen and Kirchhoff, in 1877, the first award of the Davy Medal was made in recognition of their researches and discoveries in spectrum analysis.

Another English honour conferred upon him was that of the award in 1898 of the Albert Medal of the Society of Arts, given for "distinguished merit in promoting art, manufactures, or commerce," in recognition of his numerous and most valuable applications of chemistry and physics to the arts and to manufactures.

On the motion of Professor ODLING, seconded by Dr. E. ATKINSON, a vote of thanks was passed to Sir HENRY ROSCOE for his Lecture.

Ordinary Meeting, April 5th, 1900.

Prof. J. M. THOMSON, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Ashton, Land Hill House, Hoscarr Moss,

Ormskirk, Lancs.; Richard Henry Cyril Gompertz, 110, Elgin Crescent, Notting Hill, W.; Alexander Ernest McKensie, 11, Bank Road, Workington; Hugh McNair, Bellfield, Wishaw; Herbert Procter Smith, 60, Stepney Street, Llanelli; George Edward Tomlins, 4, Radford Road, Hither Green, London, S.E.

Of the following papers, those marked * were read:—

*53. "The Liquefaction of a Gas by 'Self-cooling.'" A Lecture Experiment." By G. S. NEWTH.

The principle of the modern method for obtaining liquid air or oxygen by the "regenerative" method may be illustrated for lecture purposes by means of nitrous oxide, the spiral of fine copper tube being attached directly to the steel bottle containing nitrous oxide, and inserted into a Dewar vacuum-jacketed test-tube. No other insulating arrangements are required. In order to maintain the necessary pressure in the nitrous oxide bottle the latter is kept in warm water at a temperature of about 30°.

*54. "Note on Partially Miscible Aqueous Inorganic Solutions." By G. S. NEWTH.

When strong aqueous ammonia (sp. gr. 0.880) is added to a saturated solution of potassium carbonate and the liquids shaken together, two distinct layers separate out, just as in the case of water and ether. At ordinary temperatures, it is found that the potassium carbonate solution dissolves about 37 per cent of the ammonia solution, while the latter dissolves about 6 per cent of the potassium carbonate solution by volume.

The solubility of each liquid in the other increases with rise of temperature, the curves of their solubilities intersecting at 43°, above which temperature the solutions are miscible in all proportions. A small amount of added water is also found to increase the mutual solubility; with 12.9 per cent of added water, the separate phases cease to exist above 10°, whilst if 18.1 per cent of water be added, the liquids are miscible in all proportions at all temperatures above 0°. When cooled below these critical temperatures, the clear solution instantly becomes turbid by the separation into two liquids. No other aqueous solutions of inorganic substances have as yet been found which exhibit a similar behaviour, but strong aqueous solutions of trimethylamine and triethylamine behave in a like manner with a saturated solution of potassium carbonate.

DISCUSSION.

Dr. DIVERS said that Mr. Newth's paper was interesting on account of the evidence it afforded that we had in aqueous ammonia an analogue of aqueous alcohol, the liquefied ammonia precipitating salts from aqueous solution and becoming dehydrated by potassium carbonate. He had himself shown that ammonium nitrate deliquesced in ammonia gas just as other salts deliquesced in aqueous vapour, and then furnished liquid ammonia under atmospheric pressure, which behaved as a solvent like water or alcohol.

*55. "The Decomposition of Chlorates. Part II. Lead Chlorate." By WILLIAM H. SODEAU, B.Sc.

The preparation of pure anhydrous lead chlorate and the examination of the products of its slow decomposition were first dealt with. The solid residue was found to absorb chlorine very readily at the temperature of the decomposition (about 200–240°), hence much of the chlorine first evolved is usually re-absorbed.

When quantities of 1 grm. were decomposed at atmospheric pressure in times varying from fifteen to sixty-five minutes, the chlorine given off varied from 45 to 60.6 per cent of the amount originally present in the chlorate actually decomposed. The employment of a stream of nitrogen increased this proportion, the series of experiments thus carried out pointing to 87.5 per cent of chlorine as the limiting value when re-absorption is entirely eliminated, although Spring and Prost (*Bull. Soc. Chim.*, 1889, [iii], 1, 340), obtained only 8 per cent in the decomposition of large quantities. Only 81.4 per cent

could be obtained by reducing the pressure to 2 m.m., but this is probably accounted for by the necessary increase of temperature having facilitated re-absorption; it seems remarkable that decrease of pressure should markedly impede the decomposition of the chlorate. Addition of lead chloride appears to have no effect whatever.

In violent decompositions (lasting about one second) at atmospheric pressure, some oxychloride was formed, and only about 39 per cent of the chlorine was obtained. Similar decompositions at pressures varying from 6 to 20 m.m. gave 58.5 per cent, but the much higher temperature must no doubt have prevented the re-absorption from being even then successfully eliminated.

The author concludes that the slow decomposition of lead chlorate consists of two independent reactions: (1) $\text{Pb}(\text{ClO}_3)_2 = \text{PbCl}_2 + 3\text{O}_2$; (2) $\text{Pb}(\text{ClO}_3)_2 = \text{PbO}_2 + \text{Cl}_2 + 2\text{O}_2$, the latter having about seven times the velocity of the former. At the same time, the reaction $\text{PbO}_2 + \text{Cl}_2 = \text{PbCl}_2 + \text{O}_2$ proceeds to a greater or less extent according to the conditions, and may result in much of the chlorine being re-absorbed. The mechanism in rapid decomposition is probably similar, except that the higher temperature decomposes much of the peroxide giving oxychloride.

*56. "The Bromination of Benzeneazophenol." By J. T. HEWITT and W. G. ASTON.

One of the authors recently (*Trans.*, 1900, lxxvii, 99), described the nitration of benzeneazophenol with dilute nitric acid at 40–45°. The production of benzeneazo-o-nitrophenol agree with the formulation of benzeneazophenol as a hydroxylic derivative of azobenzene, but was not compatible with the structure of quinonephenylhydrazine. Shortly after the publication of these results, a note by Professor Armstrong (*Proc.*, 1899, xv, 243), appeared in which it was stated that bromine and benzeneazophenol yielded a product giving *p*-bromoaniline and phenol on reduction. The authors find, however, that the first product of the action of bromine on benzeneazophenol is benzeneazo-o-dibromophenol, if the bromination is carried out in acetic acid solution to which sodium acetate is added in order to prevent any formation of quinonephenylhydrazine hydrobromide. In fact, with the exercise of care in the matter of cooling, and the slow addition of the acetic acid solution of bromine, a nearly quantitative yield may be obtained, the substance separating immediately in a very pure condition.

Benzeneazo-o-dibromophenol melts at 136° (corr.); it forms a well crystallised sodium salt, but no hydrochloride or hydrate has been obtained, although it gives a sulphate with concentrated sulphuric acid.

The acetyl derivative melts at 143°, the benzoyl derivative at 120°, and the ethyl ether at 71°. The latter compound does not show any mobility of its bromine atoms, boiling for one hour with acetone leaving it unchanged. The substitution of other azophenols is being investigated.

*57. "A New Glucoside from Willow Bark." By H. A. D. JOWETT, D.Sc.

Having had occasion to examine a bark purchased as that of black willow, which could not be further identified than as some species of *Salix*, it was found that the glucoside contained in the bark was not salicin, but a new compound. Chemical examination has shown it to be the glucoside of *m*-oxybenzaldehyde, and the name *salinigrin* is provisionally suggested for it. It is contained in the bark to the extent of about 1 per cent, and is a white, crystalline substance melting at 195° (corr.).

It is soluble in 52.2 parts of water and in 218.2 parts of alcohol at 15°, and is laevorotatory $[\alpha]_D^{15} = -87.3^\circ$. From salicin, it is sharply distinguished by yielding a colourless solution with sulphuric acid, salicin under similar conditions producing a blood-red colour. Its formula is $\text{C}_{13}\text{H}_{16}\text{O}_7$, and it splits up, on hydrolysis, into *d*-glucose and *m*-oxybenzaldehyde.

*58. "Alkylation by Means of Dry Silver Oxide, and Alkyl Iodides." By GEORGE DRUCE LANDER, D.Sc.

In addition to the results given (*Proc.*, 1900, 6), the following were described: By the action of dry silver oxide, and ethyl iodide on acetanilide, ethyl *i*-acetanilide, $C_6H_5N:C(OC_2H_5)CH_3$, is produced. This is a colourless, mobile liquid, boiling at 207–208°, easily hydrolysed by mineral acids into aniline, acetic acid, and alcohol. By warming with aniline, diphenyl ethenyl amidine, $PhN:C(NH\cdot Ph)CH_3$ (m. p. 131–132°) is formed.

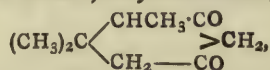
Ethyl malonate, by prolonged boiling with an excess of oxide and ethyl iodide, is partially ethylated, nearly 8 grms. of ethyl ethylmalonate being obtained from 32 grms. of ethyl malonate.

The action of silver oxide and methyl iodide on salicylic acid gave methyl methoxybenzoate boiling at 245°; the free acid melted at 99°.

Oxidation may also occur, as in the following cases: In alkylating benzoin, part is oxidised to benzaldehyde and benzoic acid, the latter being then alkylated. In the alkylation of ethyl acetoacetate, if the iodide be added to the mixed ethereal salt and oxide, a small quantity of a high boiling oxidation product, probably ethyl diacetyl-fumarate, is formed, which crystallises from ether in fine needles (m. p. 102–105°).

59. "The Interaction of Mesityl Oxide and Ethyl Sodiomethylmalonate." By ARTHUR WILLIAM CROSSLEY.

By the condensation of mesityl oxide with ethyl sodiomethylmalonate, ethyl trimethyldihydroresorcinol, $C_{12}H_{18}O_4$, is obtained, which separates from a mixture of chloroform and light petroleum as a microcrystalline powder melting at 94°. On hydrolysis with alcoholic potash, it yields trimethyldihydroresorcinol,—



which crystallises in clusters of needles melting at 99.5–100°. The ethyl ether, $C_{12}H_{18}O_4$, is a faintly yellow oil boiling at 264–265° (750 m.m.), and the silver derivative a white, flocculent precipitate.

By oxidising the resorcinol with sodium hypobromite, it is converted into an acid having the formula $C_8H_{14}O_4$, which melts at 88°, and seems to be $\alpha\beta$ -trimethylglutaric acid. If the oxidation be arrested before it is complete, a dibromo- and a monobromo-derivative may be obtained. The former, having the formula $C_9H_{12}Br_2O_2$, crystallises from alcohol in needles melting at 112.5°, and the latter $C_9H_{13}BrO_2$, separates from benzene in glistening plates melting with decomposition at 152°.

The more complete investigation of the properties and reactions of the resorcinol and its derivatives is in progress.

60. "The Products of the Action of Fused Potash on Dihydroxystearic Acid." By HENRY RONDEL LE SUEUR.

From the products resulting from the fusion of dihydroxystearic acid (m. p. 130.5–131°) with potassium hydroxide at a low temperature, two acids have been isolated. One of these is a dibasic acid, $C_{18}H_{34}O_5$, which crystallises from acetic acid in aggregates of long, flat needles melting at 111–111.5°. The silver salt, $C_{18}H_{32}O_5Ag_2$, is a white, curdy precipitate, the calcium salt crystallises with $3H_2O$, and the ethyl salt, $C_{18}H_{32}O_5Et_2$, is a slightly yellow, oily liquid boiling at 269–270° under 30 m.m. pressure. The other acid, $C_{18}H_{34}O_3$, crystallises from dilute alcohol in small plates melting at 78.5–79°, and is probably identical with the acid which Saytzeff (*Journ. Prakt. Chem.*, 1886, xxxiii., 300), obtained in an impure state by the distillation of dihydroxystearic acid.

If the fusion of the dihydroxystearic acid be carried out at a higher temperature, the main products formed are azelaic acid, pelargonic acid, and an oil which boils at 280–300° under 50 m.m. pressure.

The author intends to investigate thoroughly the various products obtained by fusing the dihydroxystearic acid from oleic and elaidic acids) with alkalis, and to study generally the action of fused alkalis on hydroxylated fatty acids.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 14, April 2, 1900.

A New Gaseous Body: Sulphur Perfluoride, SF_6 .—H. Moissan and P. Lebeau.—When a small piece of sulphur, supported by a fine platinum wire, is pure in an atmosphere of fluorine above mercury it takes fire, burning with a livid flame, and the mercury rises in the tube. The resulting gas is found to be not absorbed by water and partially absorbed by potash solution. The gas remaining after treatment with alkalis is very stable. These preliminary experiments show that two substances have been formed:—(1) A gaseous body, which is unattacked by water, but absorbed by potash; (2) a gaseous body, unabsorbed by water and alkalis, but able to be destroyed by sodium vapour. Further examination shows that these two sulphur fluorides are always formed together, but, by varying the proportions of sulphur and fluorine, a gas containing 90 per cent of the perfluoride (the portion unattacked by alkalis) is formed. The authors examine the properties of this mixture.

Action of Hydrogen on Antimony Sulphide.—H. Pélabon.—At temperatures above 360°, hydrogen acts on crystallised antimony sulphide, giving sulphuretted hydrogen and antimony. Under the same conditions of temperature, sulphuretted hydrogen attacks antimony, forming the triarsulphide, Sb_2S_3 . If the operations take place in sealed tubes, the two inverse reactions tend to a system of four bodies in chemical equilibrium. A study of this system leads to the conclusion that the limiting composition of the gaseous mixture depends only on the temperature. The value of p increases with the temperature, and this is in perfect harmony with the law of the displacement of equilibrium by temperature, if it is admitted that, under the conditions of the experiment, the reaction $Sb_2S_3 + 3H_2 = 3H_2S + 2Sb$ is, as at 15°, accompanied by an absorption of heat.

Nickel Arsenide.—Albert Granger and Gaston Didier.—A nickel arsenide, Ni_3As_2 , intermediate between those of the two sub-arsenides (Ni_2S , described by Gehlen and Berthier, and natural arsenide, $NiAs$), was prepared by treating pure nickel with arsenic chloride.

Tungsten Biphosphide.—Ed. Defacoz.—The action of dry gaseous hydrogen phosphide on tungsten hexachloride at a temperature of about 450°, allows of the preparation of a definite new compound—the biphosphide, WP_2 . The author studies the properties of this body, and from it prepares the following compounds:—A chloro-phosphide, a double phosphide, and another simple phosphide.

A New Terpenic Alcohol and its Derivatives.—P. Genyresse.—Pinene, under the influence of nitrous vapours or nitrogen peroxide, gives a secondary alcohol, pinenol, which is characterised by its acetic ether, its ketone, and the oxime of this latter. The author has not yet assigned a definite formula for this new body.

Action of Isocyanate of Phenyl and Isothiocyanate of Phenyl on Bibasic Acids.—Elophé Bénech.—It is known that phenyl isocyanate acts on succinic, glutaric, and camphoric acids. M. Haller first obtained the anhydrides of the acids, then the phenylsuccinimide, on one hand, and the glutaric and camphoric dianilides on the other. These derivatives, heated to a high temperature, yield the corresponding imides. The author attempts to generalise this reaction, so as to deduce a general process for the preparation of dianilides corresponding to bibasic acids.

Journal de Pharmacie et de Chimie,
Series 6, Vol. xi., No. 1.

A New Method for the Acidimetric Estimation of Vinegar.—M. Durieu.—The following method has given good results with coloured vinegars. Two solutions are prepared:—1. Carbonate of soda, at 5 per cent. 2. Glacial acetic acid, at 7 per cent. The apparatus required is:—A tube graduated in tenths of a c.c., as used in Esbach's method for the estimation of urea, and a 1 c.c. pipette. 6 c.c. of the alkaline solution are first poured out, so as to have an excess of bicarbonate; then 6 c.c. of alcohol at 95°, the liquids not being mixed; we then add 1 c.c. of the acetic liquor; the total volume then measures twelve divisions; close the tube with the thumb, and shake. When the reaction is finished, the tube is placed in a vessel full of water, and shaken as in estimating urea; the second reading is 19.5, for example. A similar operation is effected with the vinegar under examination, after making quite certain that it does not contain any acetic acid, and a second reading is obtained, say 18.4; by a simple calculation the proportion of acid is found to be 59.70 grms. per litre. The advantages of this method are that no new apparatus is required, and it is of great sensitiveness; it is, however, of great importance that the liquids be accurately measured, and, above all, the the alcohol must not be replaced by water.

No. 2.

This number contains no matter of chemical interest.

No. 3.

Action of Iodine on Antipyrine.—J. Bougault.—The author has already described a method for the estimation of antipyrine by iodine; the present paper has for its object the applications of this method and the examination of the processes of the reaction. The method can be used for the estimation of hypnol and salipyrine, exactly in the same way as for antipyrine; it suffices to remember that 1 grm. of hypnol corresponds to an absorption of 0.7185 grm. of iodine, and 1 grm. of salipyrine to 0.7791 grm. of iodine. It cannot, however, be used for all the compounds of antipyrine. The compound of antipyrine formed during the reaction is monoiodantipyrine, which again forms very complex compounds with the mercuric salts. When we act molecule for molecule with iodine on antipyrine, in the presence of mercuric sublimate in alcoholic solution, it appears that the antipyrine first fixes the iodine, forming an unstable product of addition, which then loses 1 molecule of HI, giving monoiodantipyrine; thus this HI would decompose a corresponding quantity of HgCl_2 , giving HgI_2 and HCl.

On Iodantipyrine, $\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O}$.—J. Bougault.—Iodantipyrine is obtained pure from the compound $(\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O})_4\text{HgI}_2\text{HgCl}_2\text{HCl}$, which is treated with a solution of iodide of potassium made alkaline with carbonate of sodium; the substance is dissociated, the HgI_2 , HgCl_2 , and HCl passing into solution, and the insoluble iodantipyrine remaining. Estimation of the I confirmed the identity of this body:—

I.	II.	Theory for $\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O}$.
Iodine = 40.45	40.63	40.44

The solubility is 0.080 grm. in 100 c.c. of water. Iodantipyrine can also be prepared by the action of iodine on antipyrine in aqueous solution in the presence of acetate of soda; the return is nearly theoretical.

The Spontaneous Formation of Crystallised Oxalate of Manganese during the Permanganic Oxidation of Citric Acid.—G. Denigès.—Ninety grms. of permanganate of potash are dissolved in 3 litres of warm water. The solution is cooled to 15–16°. We also dissolve 300 grms. of citric acid in 600 grms. of warm water, and this solution—also cooled to 15 to 16°—is added to the first, and placed in a beaker surrounded with water at 10–12°. In one or two minutes the mass changes

colour, becoming first of a yellowish-red, then brown, and at the same time giving off CO_2 in abundance, while the temperature rises to 30° or 35°. When the gas ceases to come off, the temperature is brought down to 25–28°, and the mixture left alone. After four or five days the sides of the glass become covered with small prismatic crystals, some attaining $\frac{1}{2}$ c.m. in length. The mother-liquor, which is decanted, and which previously contained a very large quantity of acetone-dicarboxic acid, no longer contains a trace. The washed and dried crystals are rarely homogeneous; the largest ones, rose-coloured and prismatic, can be easily picked out; others appear as small, white, hexagonal crystals, but both kinds have all the analytical reactions of the oxalates. The prismatic crystals gave the following results:—

	Found.	Calculated for $\text{C}_2\text{O}_4\text{Mn} + 3\text{aq.}$
H_2O (at 110°)	26.90 p.c.	27.41 p.c.
Mn (as Mn_2O_4)	38.95 "	38.76 "
C	12.15 "	12.24 "

And the white crystals gave—

	Found.	Calculated for $\text{C}_2\text{O}_4\text{Mn} + 2\text{aq.}$
H_2O (at 110°)	20.21 p.c.	20.11 p.c.
Mn (as Mn_2O_4)	42.59 "	42.66 "
C	13.30 "	13.41 "

MISCELLANEOUS.

Popular Chemistry.—The following paragraph is taken from a recent number of a popular contemporary:—"Gold, silver, steel, aluminium, and lead, when immersed in tauric acid, a new chemical discovery, becomes as pliable and ductile as putty."

The Chemists' Exhibition, 1900.—This exhibition, organised by *The British and Colonial Druggist*, will be held at Manchester on June 19th to 22nd. In addition to numerous Pharmaceutical Exhibits, the undertaking will provide examples of the progress made in Dentistry, Optics, Photography, Dietetics, Sanitation, &c. The Chemists' Exhibition is in future to be held alternately in London and the provinces; Manchester is one of the most important centres, as within a radius of a few miles round Manchester is included a population exceeding that of Greater London. Further information relative to the Exhibition can be obtained from the Managing Director, 44, Bishopsgate Without, London, E.C.; personal inquiries can be made any day between 11 a.m. and 12 noon.

Harmful Action of the Fumes of Chloride of Nitrogen.—W. Hentschel.—Accidents due to the inspiration of the fumes of chloride of nitrogen, which hardly appears to be an irritant, have not up to the present been recorded. The author, however, after having been working with solutions of NCl_3 for about six months, was suddenly attacked with inflammation and acute irritation of the mucous membrane, pains in the bronchial tubes, loss of voice, and fever; recovery was very slow. —*Berichte*, xxxii., p. 1878.

On the Density of Liquefied Gases.—A. Ladenburg and C. Krügel.—The authors have already given measurements of the densities of liquefied gases (*Berichte*, xxii., p. 46) by weighing a mass of glass in the hydrostatic balance. Prof. Dewar having made similar experiments by weighing metallic masses, they have repeated their measurements by weighing a mass of silver. In this manner they obtained figures about 3 per cent lower than those previously found,—in fact, very close to those found by Prof. Dewar. They found the density of liquid oxygen, $D = 1.134$. For liquid air containing x per cent of oxygen, they found $D = 0.86 + 0.00289x$. The density of liquid ethylene is 0.6095. They at first thought

that the disagreement between the new and the old results was caused by an inexact determination of the coefficient of expansion of the glass or of the silver at very low temperatures; it has, however, been verified that this is not the case, so that at present the discrepancy cannot be satisfactorily explained.—*Berichte*, xxxii., p. 1415.

Peroxidised Compounds.—P. Melikoff and L. Pissarjevsky.—Theoretical considerations of the peracids and peroxides have led to the following conclusions:—1. The peracids are compounds of the type H_2O_2 . When treated with concentrated SO_4H_2 , they give off ozone like the peroxides. 2. The compounds of the peroxides with H_2O_2 are entirely comparable with the hydrates of the oxides. 3. These compounds, brought into contact with the peracids give, by double decomposition, water and salts of the peracids and peroxides.—*Journ. Soc. Phys. Chim. R.*, xxxi., p. 273.

MEETINGS FOR THE WEEK.

TUESDAY, May 1st.—Royal Institution, 3. "Studies in British Geography," by Hugh Robert Mill, D.Sc., LL.D., F.R.S.E.

Royal Institution, 5. Annual Meeting.

WEDNESDAY, 2nd.—Society of Arts, 8. "Some Unfamiliar Masterpieces of the Italian School," by Miss Halsey.

THURSDAY, 3rd.—Royal Institution, 3. "A Century of Chemistry in the Royal Institution," by Prof. Dewar, M.A., LL.D., F.R.S.

Chemical, 8. "Brazilin" (Part IV.), by A. W. Gilbody, W. H. Perkin, jun., and J. Yates. "Hæmatoxylin" (Part V.), by W. H. Perkin, jun., and J. Yates. "The Substituted Nitrogen Chlorides and Bromides derived from *o*- and *p*-Acet-toluidine, and their Relation to the Substitution of Halogens in Toluides and Toluidines," by F. D. Chattaway and K. J. P. Orton.

FRIDAY, 4th.—Royal Institution, 9. "Pottery and Plumbism," by Professor T. E. Thorpe, LL.D., D.Sc., Ph.D., &c.

SATURDAY, 5th.—Royal Institution, 3. "Egypt in the Middle Ages," by Prof. Stanley Lane-Poole, M.A.

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MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. LXXXI., No. 2170.

ON KRYPTON.*

By Profs. A. LADENBURG and C. KRUEGEL,
of Breslau.

AFTER much work with liquid air, and many researches on the measurement of low temperatures and the separation of bodies by this means, we consider we are in a position to solve a few questions which have been raised by the splendid researches and discoveries of Ramsay and his co-workers. It seemed to us possible to obtain krypton, of which only little was known at the time we began these labours, in a state of greater purity, and to settle somewhat more accurately its properties, specially also to prove if its atomic weight really amounts, as Ramsay assumes, to 80-82.

The beginning of this work goes back more than a year, as the first large quantity of liquid air which we could obtain (in March of the past year) was lost in transport, and we were only placed in the position to replace this last autumn. In the meantime Ramsay has also worked up larger quantities of liquid air for krypton, as we are informed by the report which appeared in the *Chemiker Zeitung* of the Munich Congress of Physicists. Still there has appeared no authentic publication on krypton (at least known to us) since the first publication in the *Comptes Rendus* (see also *Zeitschrift für Physikalische Chemie*, xxvi., 362) and the Address published by Ramsay in the German Chemical Society (*Deutschen Chemischen Gesellschaft*, December, 1898), so that we saw no ground for interrupting the work once begun.

After we had learned that the factory Rhenania, near Aachen, had erected a Linde's air-liquefying machine capable of furnishing 50 litres of liquid air per hour, we entered into negotiation with them, and we were permitted to utilise for our purpose the residue of evaporation from 1000 litres of liquid air. Unfortunately there occurred many interruptions in the management of the machinery, so that it was three weeks before a quantity of 850 litres liquid air was gained, of which one of us (K.) brought here as much as 3 litres of the evaporated residue in two of Dewar's flasks, where we collected the gas as it evaporated in large gasometers. We obtained 2300 litres of gas, which were freed from oxygen by passing over red-hot copper. From the remaining 120 litres the nitrogen was separated by essentially the methods mentioned by Lord Rayleigh and Ramsay for the isolation of argon. The last portions of the nitrogen were always oxidised by sparking with surplus oxygen over soda-lye, and the remaining oxygen was absorbed with pyrogallol and soda. In this way a nearly complete separation of the oxygen was obtained, as when treated with yellow phosphorus only a very slight absorption was recognisable.

For sparking over soda-lye we have had made glass vessels of the form shown in Fig. 1, which have answered very well.

From these vessels the gas, after being dried with anhydrous phosphoric acid, was collected into several of Ramsay's gasometers.† In such operations it is self-evident that all intermediate parts must be pumped quite airless, for which we used a Stuhl's mercury air-pump, which worked to our great satisfaction.

In this way there were finally obtained 3.5 litres gas, which then were condensed in liquid air. The condensing vessel which contained wires fused in, and the

junction of the thermo-element, serving as thermometer, had the annexed form (see Fig. 2), and was pumped completely air empty before the gas was let in. The gas condensed itself very easy and complete under somewhat raised pressure (which is obtained by the raising of the mercury reservoir which is connected with the gasometer) to a transparent colourless fluid, in which floated small numbers of colourless crystals.*

Now the liquefied gas was raised to boiling-point by raising the condensing vessel out of the liquid air, and was fractionated into various gasometers, according to the boiling temperatures.

The temperature rose quickly from -189° to -181.2° ; there it became tolerably constant, and about 2.5 litres of gas were here collected in bottles 2, 3, and 4, whilst bottle 1 contained that boiling between -189° and -181° . Then the temperature rose quickly to -153° , where the last portions of fluid evaporated. This part was collected in bottle 5. Finally, there remained a crystalline residue, which melted at about -147° ,† and then quickly evaporated, and was collected in bottle 6.

Fig. 1.

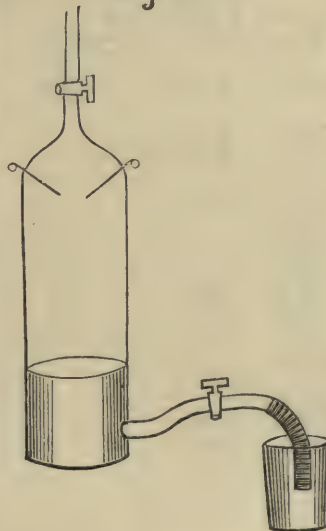
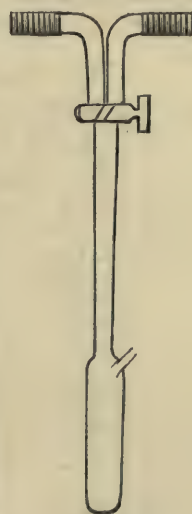


Fig. 2.



The gases from bottles 2, 5, and 6 were now examined with regard to their density, and also as to their spectrum characters.

Gas from bottle 2 (boiling-point -181.2°). This showed a very complete argon spectrum, in addition there was plainly visible the green krypton line, but not the yellow. The density of the gas was next found to be 38.6. But after the gas was mixed again with O, and sparked over soda-lye, then freed from O and dried, it showed a density of 40.34.

Gas out of bottle 5 (boiling-point -170° to 153°). Here also there was a beautiful argon spectrum, but on it was seen a very distinct krypton spectrum, in which the line D_4 and the green line were brilliant. The determination of its density gave 42.21 ($O=32$), from which it follows that we have to deal with a mixture of argon and krypton, in which the first forms the principal part.

The examination of the gas out of bottle 6 furnished unexpected results; here we saw a strong krypton

* Argon also condenses easily in liquid air at about $1\frac{1}{2}$ atmospheres. The boiling-point at normal pressure (745 m.m.) is between -181.2° and -178° (compare against this, Olszewski, *Zeit. für Phys. Chem.*, xvi., 383). The inconstant boiling-point corresponds to the complete nature of argon.

† This melting-point determination can only be looked on as a provisional one, as the mass of the body was not sufficient to carry out an exact determination.

* Communicated by Hrn. van't Hoff to the Berlin Academy of Sciences.

† See *Zeitschrift für Physikalische Chemie*, xxviii., 247. These are especially suitable for such purposes.

spectrum in which the lines D_4 , $586.9 \mu\mu$, and the green line $558.1 \mu\mu$ were brilliant, like hydrogen lines. Besides, there were several very faint lines, which we were inclined to consider as argon lines. The question whether argon was really present appeared to us of importance, and its affirmation was so much more doubtful, as the characteristic argon line, according to our estimation, the orange line $603.3 \mu\mu$, as also the most refrangible violet lines, were totally absent. We have therefore submitted our krypton spectrum to an accurate examination, and have measured a large number of lines, using a spectrometer which admitted of a reading to half a minute. We add here in column I. the red argon spectrum measured by Crookes; in column II. the argon spectrum measured by us; in column III. our krypton spectrum, and, finally, in column IV. the krypton spectrum mentioned by Ramsay and Travers, concerning which we may remark that in the latter are left out the argon lines observed at the same time (compare *Zeit. fur Phys. Chem.*, xxvi., 363).

It is seen on comparison that ten lines of our krypton spectrum, of which seven are in the red, are identical with argon lines, but that several of the fainter argon lines, together with the whole violet end of the argon spectrum, do not occur in our spectrum. As it appears to us, one must conclude therefrom that either very little argon or only a constituent part of argon is contained in our krypton.

	Argon. I.	Argon. II.	Krypton. III.	Krypton. IV.
Red.	764.6	764.4		
	750.6	749		
	737.7	738.3		
	726.3	726.7		
	—	716.3		
	—	715.3		
	705.64	708.8	707.6	
	696.56	697.3	697.3	
	684.2	688.9		
	675.4	676		
Orange.	666.4	669.2		
			645.2	
	640.7	642.3		
	637.7	638.3	638.1	
	630.2	631.9	631	
	628.1	—		
	621.0	623.2	624.3	
	617.3	617.1	617.8	
	614.3	614.6		
	609.9	610.6		
Yellow.	605.6	605.7	608.3	
	604.5	—	605.7	
	603.8	603.3		
			601.45	601.1
			599.2	—
	593.5	—		
	592.6	—		
	590.9	590.7		
	588.7	—	586.9	586.77
	585.8	—		
Yellow-green.	583.4	—		
	580.3	—	—	582.9
	577.1	—		
	574.6	574.8		
	568.3			
	565.1	565.5	565.9	—
	561.0	561.3		
	556.7	557.6	558.1	556.8
	555.7	556.8	557.3	556.0
	552.0	—		

	Argon. I.	Argon. II.	Krypton. III.	Krypton. IV.
Green.	549.65	—		
	545.6	546		
	544.4	—		
	542.1	542.5		
	525.8	525.6		
	522.2	522.0		
	518.58	519.2		
	516.5	516.5		
	506.5	—		
	501.2	—		
Green-blue.	496.55	—		
	493.8	—		
	487.9	—	492	490.9
	—		491.3	
			484.0	483.4
			482.5	483.0
		481.5		
			480.5	480.7
			473.6	473.6
			470.0	—
Blue.	470.12	470.6	467.5	467.1
	462.95	463.3	462.3	—
	459.45	459.7		
	451.4	—		
	450.95	451.6	450.5	—
			446.6	
			445.5	446.1
			437.5	438.7
			436.4	—
Violet.	434.5			
	433.35	433.7		
	430.05	430.2	432.5	431.7
	427.2	427.5		
	426.6	426.8	427.8	—
	425.95			
	425.15			
	420.10	420.5		
	419.8			
	419.15	419.2		
	418.3	418.4		
	416.45	—		
	415.95	416		
	415.65			
	404.4			
	394.85			
	390.45			
	383.55			
	377.15			
	363.25			
	362.37			
	362.28			
	360.50			
	356.65			
	356.28			
	355.45			

The density determination of our gas gave the figure 58.81 relative to oxygen 32. The observed data were the following:—

Weight of the gas, 0.0391 .

Volume of the globe, 16.364 c.c.

Reduced barometric pressure, 739.4 m.m.

Temperature, 19° C.

In view of the small quantity of gas and that the accuracy of our balance does not exceed 0.0001 grm., we estimate the error of our determination at 1 per cent.

For the control of this density determination, the result of which very much surprised us, we mixed the gas anew

with oxygen, and sparked over soda-lye. Hereby occurred a not inconsiderable volume reduction, so that we believed that our gas still contained nitrogen. But later it came out that our oxygen, which we considered nitrogen free, was not quite pure.

But we must here expressly point out that we now sparked so long that even after some hours no decrease of volume occurred, so that we could be sure that we had no more nitrogen in our gas.

Then it was freed from oxygen with pyrogallol and soda, and collected over mercury, where it was left standing over yellow phosphorus and fresh fused soda for forty hours. After this a new determination of density was carried out. The data were now the following:—

Weight of the gas, 0.0394.
Volume of the same, 16.364 c.c.
Temperature, 17.5°.
Barometer reduced, 743 c.m.

Therefrom the density comes out (referring to O=32), at 58.67, in remarkable accord with the first found figure, 58.81.

Therefrom it follows with certainty that the krypton contained no more oxygen, and since very little argon was mixed with it, as already inferred from the spectrum examination, one may well consider it as nearly pure. This conclusion is essentially supported by the fact that this gas originated from a crystalline body, which doubtless speaks for its not being a mixture.

Then comes the question, what position does krypton occupy in the periodic scale if we consider the density 58.8 as nearly correct? We believe that we should place the new group of elements in air before group I., so that He=4 before lithium, Ne=20 before sodium, A=39 before potassium, and, finally, Kr=59 before copper.

Still this is only a hypothesis which requires further testing. Herewith we are busy, as perhaps through the solid condition of krypton there offers a newer and much more simple road for its preparation, which we have already entered upon.

This consists in the working up of the well separated constituents of the liquid air which evidently will contain krypton next to carbon dioxide, when the solubility in liquid air does not suffice to hold in solution all the krypton present.

OBSERVATIONS ON THE EFFECT OF DESICCATION OF ALBUMIN UPON ITS COAGULABILITY.*

By J. BRET LAND FARMER, M.A., Royal College of
Science, London.

IT has been known for some time that it is possible, under certain circumstances, to expose seeds to the influence of high temperatures without thereby necessarily destroying their power to germinate. Some experiments in this direction were conducted at the Royal Gardens, Kew, some years ago by Dr. Morris, but the results, although of much interest, do not appear to have been published. However, the seeds were exposed to the action of boiling water, and even to a higher temperature in an oven, without losing their ability to germinate when the ordeal was over.

It has been noticed, in heating seeds in water, that if the seed-coat through any cause becomes ruptured, or if it softens and swells, the seeds which are thus affected are incapable of manifesting any further evidence of vitality. It appears to me that a fair inference to be drawn from these facts is that the admission of water to the living cells is a potent factor in bringing about their death.

Jodin (*Comptes Rendus*, 1899) has recently communi-

cated some facts which point to the same conclusion. He exposed seeds of pea and cress to a temperature of 98° C., and found that, unless great care had been previously exercised to ensure the dryness of the seeds, they were all killed. When they had been previously dried he succeeded in subsequently germinating 30 per cent of the peas and 60 per cent of the cress seeds. Perhaps the disproportion in favour of the latter may, at least in part, be ascribed to their small size, and consequently to the less difficulty in sufficiently drying the seeds.

It would seem to follow, from what has been said, that the instability of the complex molecular structure of which living organisms are made up may be lessened by appropriate desiccation, but the substances concerned are too complex to render themselves readily accessible to inquiry. It appeared, however, that it might be worth while to study the effects of desiccation on albumin from this point of view. Albumin is not only a highly complex proteid, and perhaps in some respects akin to protoplasm itself, but it is one which gives tolerably definite heat reactions. It is in connection with the last-mentioned point that the new facts in this paper are specially concerned.

It is of course known that albumin in a watery solution is readily coagulated on heating to a certain temperature. This temperature, however, is not necessarily constant for even one type of albumin, doubtless owing to the readiness with which it undergoes change. Thus albumin obtained from different hens' eggs will often be found to coagulate at different temperatures, and the differences appear—in part, at any rate—to be connected with the age of the egg. I have found, in the case of freshly-laid eggs, that the characteristic opalescence which marks the early stages of coagulation may set in as low as 60° C., the clotted coagulum being fully formed at 64° C. The heat was applied by means of a large water-bath, so as to ensure its being as uniform as possible. Another sample of albumin from a different egg, tried simultaneously and under the same conditions, only exhibited opalescence at 65.6° C., and coagulated completely at 68° C.

The albumin on which most of my experiments were made was obtained from Merck, of Darmstadt, and was sent as dried egg-albumin. It readily dissolved in water, with the exception of a little flaky insoluble portion, which was filtered off. The solution had a low coagulation-point, the opalescence appearing at 60° C., and the clot at 62° C. to 63° C.* Filtering off the clot and testing the filtrate at higher temperatures yielded no further coagulation.

If a sample of this (dry) albumin be placed in a flask, the mouth of which is furnished with a cork and attached to a set of drying tubes, and the temperature of the flask raised to 80° C., a short exposure, of at any rate two to three hours, is enough to completely alter the albumin. The object of the drying tubes is to prevent any more moisture than is already present in its substance reaching the albumin from the steam or from any other source. Thus heated, the albumin is found to have become insoluble in water, and in fact to have undergone a change corresponding to coagulation.

If, however, the albumin be carefully dried before being subjected to these conditions, the results are quite different. For the present purpose it was found to be sufficient to expose a thin layer of albumin in a glass dish to a temperature of 52° to 55° C. in an incubator. This ensures a very thorough desiccation. The process may be hastened by introducing a vessel of sulphuric acid, though this precaution was not found to be necessary. Thus dried, the albumen loses its shellac or glue-like appearance, and easily crumbles to very small particles.

On comparing the solubility and coagulability of this

* It is of course known that several factors affect the coagulation-point. The figures given represent those obtained in my experiments, which were all kept as uniform as possible so as to eliminate the factor of variability.

* A Paper read before the Royal Society, April 5, 1900.

specially dried material with the ordinary sample, no difference could be detected in any respect.

Numerous experiments were made with this dried material, of which the following may be taken as typical. It may be added that the results throughout were almost surprisingly uniform in the different experiments made.

A sample of the specially dried albumin was introduced in a flask so as to form a thin layer over the bottom. The flask was connected with drying tubes filled with calcium chloride, and with phosphorus pentoxide. The flask was warmed and cooled rapidly several times, in order to cause the contained air to circulate through the drying tubes.

The temperature of the flask was then raised in a brine-bath to 102°C ., and kept at this temperature during the whole of one day (six hours). Next day, and without opening or disturbing the apparatus, the temperature was again raised to 107°C ., and finally to 110°C . It was maintained between these limits for seven hours; thus the contents of the flask had been for thirteen hours exposed to a temperature of considerably over 100°C .

On testing the albumin it was found to be soluble in water, and in no way, as far as could be observed, did it differ from the unheated material. On gradually warming the solution side by side with a similar solution of the unheated albumin, both became opalescent at a temperature of 60°C ., and both were completely coagulated at 62°C .

It thus appears that, if precautions are taken to ensure appropriate desiccation, it is possible to heat albumin for, at any rate, thirteen hours to a temperature varying between 102° to 110°C . without producing any obvious change in its ultimate molecular (or micellar?) structure. It made no difference to the result whether the heat was gradually or rapidly applied. Thus, in one experiment, the temperature was raised from 50°C . to 103°C . in fifteen minutes, and in other examples the flask was withdrawn from the hot bath, cooled, and suddenly re-immersed. How much higher the temperature could be raised without producing an obvious effect, I am not prepared to say; nor did I investigate the action (if any) which might possibly be produced by a much longer exposure to heat within the limits already mentioned. This formed no part of my object, which was primarily to try to get a point of comparison between the complex seed and the simpler but still very complex proteid.

Other experiments were made in order to test the sensitiveness of the albumin to small quantities of moisture.

For this purpose, two flasks attached to drying tubes were used, one of them serving as a control experiment, and remaining unopened until the end. The other was opened three times, and a small sample taken out each time. By this means the ordinary air of the room obtained complete access to the albumin. The duration of the experiment was ten hours. The first sample was withdrawn after the flasks had been heated to 102°C . for three hours; it dissolved and coagulated normally. A second sample was withdrawn after three hours more, and it was found that whilst it dissolved and became opalescent on heating to 60°C ., the coagulation change did not at once set in, but the opalescent solution became more milky and of a deeper fog-yellow by transmitted light, finally coagulating at about 68°C . A third sample taken out at the close of the experiment (*i.e.*, four hours after the last opening of the flask) also dissolved, became slightly opalescent at about 64°C ., but did not coagulate even at 90°C ., although the opalescent milkiness became very pronounced. Viewed by transmitted light, the solution was translucently yellow. Even boiling failed to produce anything which could be fairly termed a coagulum. It appeared probable that the admission of watery vapour had permitted the inception of the changes which normally, at high temperatures, result in coagulation; but in this case they were arrested, some precursor of alkali-albumin being probably produced, as is often the case on slowly coagulating albumin solutions. Under these circumstances, however, the entire mass of the albumin had

undergone this change. This supposition turned out to be correct, for the addition of a trace of acetic acid at once caused the solution to be susceptible to coagulation at about 60 – 62°C .* Hence it is fair to infer that although the slight amount of moisture introduced during the opening of the tube did not suffice to enable complete coagulation to occur, it did permit the early changes to begin, and to slowly, and in a modified way, to affect the entire mass. This experiment was repeated several times, and always with the same result.

It seems difficult, in the light of the foregoing observations, to resist the inference that in the complete absence of moisture albumin may be reduced to a state of relative molecular (or micellar) immobility; the re-arrangements which, in the presence of water, and at a sufficiently high temperature, normally take place in its ultimate structure being held in abeyance during the suspension of the essential condition of the presence of sufficient moisture. The substance is brought, so to speak, into a static condition; chemical or physico-chemical change is inhibited, just as is an interaction between phosphorus and oxygen when conditions of complete dryness obtain. It is tempting to extend these considerations to the case of seeds and spores, (*e.g.*, of certain bacteria), and to ask whether similar conclusions may not be fairly assumed to obtain there, for it may well be a fact that the protoplasm, like the albumin, which is at any rate akin to it, when sufficiently desiccated withstands conditions which otherwise would certainly promote chemical disintegration. They, too, appear to be reduced to a "static" condition by drying, and the researches of Romanes (*Proc. Roy. Soc.*, vol. lvii.), indicated no measurable chemical change as proceeding in them under these circumstances; and, again, the investigations of Brown and Escombe (*Proc. Roy. Soc.*, vol. lxii.), and of Sir W. Thielton-Dyer (*Proc. Roy. Soc.*, vol. lxv.), have also rendered it difficult to believe, when subjected to the other end of the scale of temperature, that any metabolism can really be proceeding. In these cases the molecular machinery of life is all present and intact, but the *manifestation of vitality*, as measured by chemical movement, and by the change in the condition of energy, is absent. But such a state differs widely from death, seeing that when the conditions favourable to the continuous progress of those reactions which are associated with vitality are restored, the organism proceeds to work in the normal manner once more. Similarly the albumin heated in the desiccated form retains, instead of changing, that particular molecular condition which enables it, on restoring the essential conditions of moisture, to coagulate in a normal fashion when heated to a suitable degree of temperature.

ON THE ESTIMATION OF THALLIUM AS THE ACID AND NEUTRAL SULPHATES.†

By PHILIP E. BROWNING.

CROOKES (*CHEM. NEWS*, viii., 243) has shown that the salt obtained by heating thallous chloride with sulphuric acid until the excess of the latter is expelled, and then raising the heat to redness, has the constitution of a neutral sulphate.

He also found that continued heating did not result in any essential loss of weight, and suggested the possibility of applying this method of treatment to the estimation of thallium.

Castanjen (*Amer. Journ. of Science*, viii., 460), in a

* A solution of albumen treated with a very small quantity of a dilute solution of potash undergoes a similar change. The substance formed is not true alkali-albumen, since no precipitate is produced on neutralising, and a coagulum on heating this neutralised solution.
† Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, February, 1900.

recent paper, discusses thoroughly the compounds of thallium, and confirms essentially the statements of Crookes in regard to the neutral sulphate, adding, however, the observation that on strong ignition in the air this salt tends to lose sulphuric acid. He also mentions in the same paper the acid sulphate, and states that on heating it first melts, and on continued heating gives off sulphuric acid, leaving the neutral sulphate.

The work to be described in this paper was undertaken to determine under what conditions the formation of these salts may be applied to the estimation of thallium. For the work a solution was made by dissolving a given amount of the nitrate in water and making up to a litre. The value of the solution was determined by precipitating measured and weighed amounts of this solution both as the iodide and chromate, as described in a previous paper (*Journ. f. Prakt. Chem.*, cii., 131). Closely agreeing results by both methods were taken as the standard. Measured amounts of this solution were drawn from a burette into weighed platinum crucibles, and the weight taken as a check on the burette reading. To the solution in the crucible a few drops of sulphuric acid was added, and the water removed by evaporation over a steam-bath. The crucible was then removed to a radiator, consisting in this work of a conical iron cup, and heated at a temperature ranging from 220° C. to 240° C., until fuming ceased and the weight after half-hour periods of heating remained constant. The crucibles were placed in a radiator upon a pipe-stem triangle so that they were about 5 cm. from the bottom, which was heated at low redness. A thermometer hung so that the bulb occupied the same position as the crucible gave the reading mentioned above.

As will be seen, the results obtained by this treatment agree closely with the calculated amounts of acid sulphate which should be formed. In several experiments this salt was dissolved in water, and the sulphuric acid present in combination precipitated by barium nitrate. The results obtained agreed closely with the formula of the acid sulphate of thallium. Having obtained by the method described the acid sulphate, the crucibles were removed and heated carefully over a free flame to low redness, when, after a considerable evolution of sulphuric acid fumes, the weight again became constant, and the results showed a condition closely approximating to that of the neutral sulphate. In several of these experiments the sulphuric acid present in combination was determined and showed amounts closely agreeing with the constitution of the neutral sulphate.

TIHSO ₄ Calculated.	TIHSO ₄ found.	Error.	Tl ₂ SO ₄ calculated.	Tl ₂ SO ₄ found.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1. 0.1605	0.1596	0.0009-	0.1344	0.1346	0.0002+
2. 0.1611	0.1608	0.0003-	0.1349	0.1346	0.0003-
3. 0.1608	0.1608	0.0000±	0.1347	0.1352	0.0005+
4. 0.1612	0.1600	0.0012-	0.1350	0.1346	0.0004-
5. 0.1602	0.1596	0.0006-	0.1341	0.1346	0.0005+
6. 0.1608	0.1596	0.0012-	—	—	—
7. 0.1617	0.1604	0.0013-	—	—	—
8. 0.1608	0.1592	0.0016-	0.1347	0.1358	0.0011+
9. 0.1609	0.1590	0.0019-	0.1348	0.1346	0.0002-

These results would seem to show that thallium may be estimated either as the acid sulphate or as the neutral sulphate by careful attention to the proper conditions of temperature.

The Hydrates of Chloride of Manganese.—P. Kouzenezoff.—The author describes a new hydrate, $MnCl_2 \cdot 6H_2O$, which is obtained by cooling a solution containing, $MnCl_2 + 11.7H_2O$ down to -21° . By shaking violently we notice the appearance of a more or less distinct cloud which slowly changes into almost colourless crystals, sometimes reaching a length of 5 m.m. This hydrate decomposes at -2° .—*Journ. Soc. Phys. Chim. R.*, xxx., 741.

THE DETERMINATION OF NICKEL IN NICKEL-STEEL.

By GEO. WM. SARGENT.

THE results obtained in this laboratory by the following method have been such as to warrant my placing it before fellow chemists, who, I believe, will find the method more reliable and more pleasant to work than most procedures now in vogue for the determination of nickel in steel.

The method in detail is as follows:—Dissolve 2 grms. of the steel in hydrochloric acid (1.1 sp. gr.), add 1 c.c. of strong nitric acid to oxidise the iron, and evaporate to hard dryness. Take up the residue in 20 c.c. of hydrochloric acid (1.1 sp. gr.), evaporate to 10 c.c. volume, and transfer the solution to a 250 c.c. separatory funnel (see method of Chase for the "Determination of Nickel and Aluminium in Steel" in the Appendix of "The Chemical Analysis of Iron," by Blair, Third Edition). Use warm hydrochloric acid (1.1 sp. gr.) for washing the contents of the beaker into the funnel, taking care to keep the volume as small as possible. Cool the funnel and its contents under the spigot, then introduce 40 c.c. of ether free from alcohol, which has just been thoroughly shaken with 5 c.c. of strong hydrochloric acid, and shake vigorously for ten minutes, keeping the temperature from rising by frequently holding the funnel under the running water. Allow the funnel to stand a few minutes, draw off the lower aqueous layer containing the nickel, copper, manganese, and other chlorides not held by the ether, wash down the sides of the separatory funnel with hydrochloric acid (1.1 sp. gr.), shake with the ether, and run the washings into the beaker with the chlorides of nickel, copper, &c. Two washings with 5 to 10 c.c. of hydrochloric acid are sufficient to completely remove the nickel and other chlorides from the funnel. The ethereal solution containing the ferric chloride is run into a residue bottle, and later the ether recovered by distillation. Boil the liquid containing the nickel to completely expel the ether and add to the boiling solution, diluted to at least 200 c.c., an excess of ammonia and 10 to 20 drops of bromine water, to precipitate any iron or manganese. Filter, wash, re-dissolve in hydrochloric acid, re-precipitate with ammonia and bromine-water, and filter. Combine the filtrates, boil, remove any precipitate, acidulate with hydrochloric acid, boil until the excess of bromine has been expelled, and precipitate the copper as sulphide. The filtrate from the copper sulphide, which contains nickel only, is evaporated to a volume of 100 c.c., cooled, and 1 c.c. excess of ammonia added. Now introduce into the nickel solution, which is best contained in an Erlenmeyer flask, 5 c.c. of silver nitrate ($\frac{1}{2}$ gm. silver nitrate in a litre of water), and the same amount of a 2 per cent solution of potassium iodide. Run into the opalescent solution, which should have a temperature slightly lower than that of the hand, standard potassium cyanide (1 c.c. equal to about 0.001 gm. of nickel) until the liquid becomes clear and bright. This titration is best made with a black background, when the end-reaction becomes very sharp and decided after a little practice, half a drop only being sufficient to discharge the opalescence (see "Determination of Nickel in Nickel-steel," by E. D. Campbell and W. H. Andrews, *Journ. Am. Chem. Soc.*, xvii., 127).

The potassium cyanide solution is standardised by introducing into an Erlenmeyer flask 10 c.c. of a solution containing a known amount of re-crystallised nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, 10 c.c. of hydrochloric acid (1.1 sp. gr.) 1 c.c. excess of ammonia, 5 c.c. each of the silver nitrate and potassium iodide, diluting the whole to 100 c.c., and running in the potassium cyanide until the solution clears. It is necessary that a blank be made upon the silver nitrate and potassium iodide used as the indicator, under the same conditions as the standardisation, and this amount deducted from each titration.

The presence of varying quantities of ammonium chloride in the nickel solution to be titrated has no effect on the titration. This is evident from the following:—

Taken.			Found.				
NH ₄ Cl pre- sent.	Ni(NO ₃) ₂ .	Weight of Ni.	Readings.		Differ- ence.	Blank.	Weight of Ni.
			First.	Second.			
Grms.	C.c.	Grm.					Grm.
1	20	0.02	0.0	20.2	20.2	0.45	0.01996
3	20	0.02	20.2	40.5	20.3	0.45	0.02007
7	20	0.02	0.0	20.2	20.2	0.45	0.01996

1 c.c. potassium cyanide solution = 0.001011 grm. nickel.

Some of the results obtained by the foregoing method I append:—

Mark.	Solution of KCN equivalent to Ni.		Weight of nickel found.		Nickel. Per cent.
	C.c.	Grm.	Grm.	Per cent.	
389	27.65	0.02795	1.397		
389	27.65	0.02795	1.397		
389	27.55	0.02785	1.392		
390	28.60	0.02891	1.445		
390	28.55	0.02886	1.443		
382	30.40	0.03073	1.536		
382	30.20	0.03053	1.527		
387	31.00	0.03134	1.567		
387	30.70	0.03104	1.552		
387	31.00	0.03134	1.567		
109	51.00	0.05156	2.578		
109	51.30	0.05190	2.595		

1 c.c. potassium cyanide = 0.001011 grm. nickel.

The above determinations were made on steels in which the manganese did not exceed one-tenth per cent, and in which there was no copper.

Different amounts of nickel were mixed with solutions containing 2 grms. of iron and the nickel determined therein:—

Taken.		Found.	
Ni(NO ₃) ₂ solution.	Weight of nickel.	KCN solution equivalent to Ni.	Weight of nickel.
C.c.	Grm.	C.c.	Grm.
30	0.03	29.60	0.02992
30	0.03	29.05	0.02937
40	0.04	39.60	0.04003
40	0.04	39.70	0.0401
45	0.045	44.05	0.0445

For the estimation of nickel in ferro-nickel, dissolve 20 grms. of the sample in aqua regia, evaporate to hard dryness, take up with hydrochloric acid (1.1 sp. gr.), transfer to a litre flask, and dilute to the mark with water. Remove 50 c.c., to which add 5 c.c. strong hydrochloric acid, and concentrate to one-sixth its volume. Transfer to the separatory funnel, and proceed as with the steel.

A sample of ferro-nickel which, by an unknown method, contained 33.93 per cent of nickel, yielded 33.80, 34.00, 33.88, and 33.96 per cent. Another sample which, according to one chemist, contained 34.95 per cent of nickel, gave 35.15 and 35.26 per cent.

The above-described method is, as can readily be seen, a combination of a modified portion of the method of Chase, with a slightly changed part of the procedure given by Campbell and Andrews. In the course pursued by Chase, two ether separations are necessary to remove the ferric chloride, while the separation, as worked by us, need not be repeated; but little ferric chloride is left, and the two ammonia precipitations are sufficient to completely remove the iron from the nickel.

With regard to the titration with potassium cyanide, that may be accomplished in the presence of most all the salts of ammonium and the mixed alkalis except the nitrates. The excess of ammonia should not in any case exceed 3 c.c. (see "Estimation of Cyanogen," by Wm. J. Sharwood, *Journ. Am. Chem. Soc.*, xix., 415).

While in steels about which one knows nothing, it will be necessary to hunt for copper, yet, in the general run of furnace work, copper is absent, and knowing such to be the case, the working with the unpleasant gas, hydrogen

sulphide, is done away with entirely. As far as time is concerned, the method is short, requiring no longer time than the method of Chase.

In conclusion, I wish to here acknowledge the assistance of Mr. Clarence Ebaugh and Mr. John K. Faust in working out this method.—*Journal of the American Chemical Society*, xxi., No. 10.

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A NEW PHOSPHATIC MANURE; PREPARED PHOSPHATE OF ALUMINA.

By M. ZECCHINI.

SOME months ago a new phosphatic compound was placed on the market under the name of *prepared phosphate of alumina*, to which was attributed an efficacy equal to that of Thomas's scoria; in fact, this new material was intended to replace the latter, and at a price, per unit of phosphoric acid, equal if not superior to that of scoria.

My advice having been sought by several companies and syndicates, with regard to this manure, I decided to carry out a few comparative culture experiments so as to learn its efficacy, and at the same time I examined its composition, as well as its behaviour under the action of the reagents most commonly used nowadays for determining the assimilability and efficacy of the phosphatic compounds as fertilising materials.

I ought to add that, in spite of my repeated enquiries with regard to the origin and source of this substance, I have not been able to obtain any information whatever on this subject. I am therefore quite ignorant as to whether it is simply a pulverised mineral or a manufacturing residue, as the word "prepared" might lead one to believe.

The material, as it exists commercially, is in a fine powder of a dirty rose-colour, with an amorphous appearance. Analysis has given me the following results:—

Water lost, between 100° and 110° ..	7.21 p. c.
Do. at red heat	0.12 "
Residue insoluble in HCl	12.63 "
Phosphoric anhydride	42.22 "
Alumina	25.45 "
Ferric oxide	11.90 "
Lime	0.35 "
	99.88 "

The part insoluble in hydrochloric acid has the following composition, in proportion to 100 parts of the original material:—

Silica	10.32 p. c.
Oxides of iron and aluminium	1.38 "
Lime	0.55 "
Magnesia	0.32 "
	12.57 "

This composition, expressed in parts per 100 of the insoluble substance, gives the following figures:—

Silica	81.71 p. c.
Oxides of iron and aluminium	10.92 "
Lime	4.35 "
Magnesia	2.53 "
	99.51 "

I ought to mention that a few qualitative analyses have shown me that I had to deal with an orthophosphate, and, further, that the material was easily soluble in hot soda or potash lye, leaving only an insoluble residue of silica and hydrate of iron.

From these analytical results we gather the following facts:—That the phosphate under examination should be considered as a neutral or basic phosphate of iron and alumina; and, secondly, that we have probably to do with a natural phosphate which has simply been ground.

There can be no doubt, however, that it cannot be looked upon as a superphosphate or a bibasic phosphate. In the first case it would contain at least 1 part of phosphoric anhydride soluble in water at the same time as the sulphates, which is not the case; but at any rate it ought to contain a large quantity of phosphoric anhydride with regard to the proportion of bases present.

The amount I found is quite insufficient to correspond with the oxides of iron and aluminium, if we wish to consider these two bodies as the neutral phosphates $\text{Fe}_2\text{P}_2\text{O}_8$ and $\text{Al}_2\text{P}_2\text{O}_8$ respectively. The quantity to effect this would be at least 45.99 per cent, while only 42.22 per cent of phosphoric anhydride was found.

It is true that a certain portion of the oxides of iron and aluminium found, might result from the partial attack of the silicate by hydrochloric acid, but the proportion would not be so great considering the amount of silica present; consequently it is very probable, as I have already stated, that we have to deal with a neutral or basic orthophosphate of alumina in which this base is partially replaced by ferric oxide.

Further, I ought to mention that the phosphates of alumina, or of alumina and iron, known as minerals,—such as wavellite, redondite, &c.,—which are, as a matter of fact, basic phosphates of alumina and iron, have the property, as has also the substance under examination, of dissolving easily in the alkaline lyes. I am therefore of opinion that it is very probable that the material I have examined should be classed as a natural phosphate analogous to those I have just mentioned.

But putting on one side this purely inductive reasoning, we come to the manner in which this material behaves with reagents which show the assimilability of phosphoric acid. With this object in view I tried the citric phosphates which are now commonly used for scoria—that is, Wagner's acid citrate of ammonia, and citric acid at 2 per cent. These two reagents were specially prepared with the necessary precautions, and were consequently perfectly fresh.

In each case I placed in a half-litre flask 5 grms. of the substance, and then added the solvent up to the mark, gently shaking to prevent it becoming stuck to the bottom, after which I subjected the flask to an hour's rotation in the well-known apparatus used for this purpose.

The quantities of phosphoric anhydride dissolved were absolutely minimal,—that is to say, 0.32 per cent with Wagner's citrate, and 1.34 per cent with 2 per cent citric acid, as means of a number of very concordant experiments.

I must not, however, pass in silence over a very curious occurrence I observed with regard to the behaviour of this phosphate with the solution of acid citrate of ammonia by Wagner's method.

Having, as I have said, made an estimation in the ordinary manner with perfectly fresh solutions properly prepared, the solubility was practically *nil*, both when using a concentrated solution (5 grms. of material to 500 c.c.) and a dilute solution (200 c.c. of solution plus 300 c.c. of water to 5 grms. of substance), as is done with scoria.

Having, then, once by accident used some acid citrate of ammonia, which had been left for some months in a flask, and which showed some mouldy growths (*penicillium*), the solubility of the phosphate increased enormously, the proportion of the substance dissolved being 25.34 per cent, although I had used the solution diluted in the proportion of 2 to 5, as is done with scoria.

I decided to repeat the experiment, so left some acid citrate, again for some months, in such a manner as to encourage the growth of moulds. I repeated the experiment under the same conditions, and obtained a still

greater quantity of the substance in solution,—that is to say, 29.95 per cent.

The fact is very curious, as the solutions remained acid; not having, however, examined the reaction any further, I am unable to offer any definite explanation. It may be possible that, by the action of the moulds, other salts of ammonia are formed having a stronger dissolving effect on the phosphate than the citrate of ammonia. I intend following up this matter.

I then conceived the idea of trying neutral citrate, such as is prepared at our agronomic stations for the examination of superphosphates. In this experiment I acted on 5 grms. of material with 100 grms. of the reagent, diluted with 150 c.c. of water, always in flasks of 250 c.c. capacity, which I submitted to rotation for an hour in the usual manner. In this way I obtained 0.86 per cent of dissolved phosphoric anhydride.

Having obtained this result in the cold, I now tried the effect of heat. I took 5 grms. of material and placed them in a flask of 250 c.c. capacity, with 100 c.c. of neutral citrate, making up the volume with distilled water. The whole was kept on the water-bath at 40 to 45° for one hour, with frequent agitation. Under these conditions 5.47 per cent of phosphoric anhydride was dissolved. As can be seen, even with neutral citrate, the solubility is low.

I then tried the use of ammoniacal citrate of ammonia, prepared according to Petermann, by reacting for an hour in the rotatory apparatus with 250 grms. of the reagent on 2.5 grms. of material. In this case the amount of phosphoric anhydride dissolved was considerable, and reached 25.79 per cent.

This fact led me to think that the solubility of the phosphate of iron and alumina depended on the alkalinity of the solution, and to decide this point I tried the following experiments:—

Into four 250 c.c. flasks I placed respectively 5 grms. of the material and 100 c.c. of standard neutral citrate. In the first I made up the volume with distilled water, while, before doing this to the other flasks, I added respectively 5, 10, and 20 c.c. of ammonia of 0.92 density. All the flasks were rotated for an hour, and after filtration I precipitated the phosphoric acid by means of magnesia mixture in all the solutions.

In this manner I obtained the following quantities of dissolved phosphoric anhydride:—

Neutral citrate alone	0.86 p.c.
Do. + 5 c.c. NH_3	18.85 "
Do. + 10 " "	31.17 "
Do. + 20 " "	31.23 "

It is thus evident that, whether hot or cold, to make any considerable proportion of this phosphate soluble, it does not suffice to use concentrated citrate of ammonia, but it is necessary for this salt to have a strongly alkaline reaction.

Taking count of this, I endeavoured to find whether the solubility of the phosphate could be still further increased by diminishing the proportion of the substance with regard to the quantity of reagent.

I therefore made two experiments in which, while maintaining the conditions of the preceding experiment,—that is to say, with 100 c.c. of standard neutral citrate in flasks of 250 c.c. capacity, and adding 20 c.c. of ammonia,—I only used 2.5 grms. of material instead of 5 grms. as before. In one of the experiments the flask was kept cold and rotated for an hour. In the other experiment I heated the flask to 40 to 45°, with frequent agitation for an hour. In the first case I obtained 31.93 per cent, and in the second case 36.67 per cent of soluble phosphoric acid.

This shows that heat aids the solution of the phosphate. In my opinion the above is the process which should be adopted in the examination of this substance, the more so as I have proved that the ordinary natural phosphates (phosphorite, apatite, &c.), reduced to fine

powder and treated in the same manner, give up to the solvent only traces of phosphoric anhydride. I will not dwell longer on this subject, nor deduce any too absolute conclusions from the practical point of view, as my firm conviction is that our reagents are badly chosen for the determination of the true fertilising value of a manure, and especially of these phosphates, as from this point of view the real proof can only be shown by experiments on culture.

In my opinion laboratory experiments should only be taken as showing the relative chemical differences in the nature of the materials examined.

It is also no less true that the behaviour of the phosphate of alumina is different to that of scoria, which is very soluble in acid citrate, in solutions of citric acid, and (as I have already had occasion to show) even in neutral citrate, while the phosphate of alumina may be looked upon as insoluble in these reagents.

Thus, the solubility in a distinctly alkaline citrate is so far removed from that which may occur in nature, by means of osmotic phenomena with the acid juices of the roots of plants, that it cannot be considered as affording much proof with regard to the fertilising value of the substance.

It should be further noted that this phosphate contains hardly any lime, even combined, and none at all free: this, without doubt, is an important coefficient of the efficacy of scoria. For this, as well as for other reasons, it seems to me that it would at present be at least premature to make an absolute comparison of this *prepared phosphate of alumina* with scoria. But this is not a sufficient reason to refuse it, *à priori*, the character of having a distinct fertilising power. It is in a very fine state of division; and in such a condition even the natural phosphates of lime, although insoluble in water and only slightly soluble in the ordinary citric solvents, and neutral or alkaline citrates, give good results in practice, especially when well mixed with the soil by thorough digging.

A sound opinion, thus, cannot be given with regard to this new phosphatic manure, except after systematic practical experiments. I have, as I have said, started such experiments, and hope soon to be able to describe the results. It seems to me, however, that it would for the present be more prudent to give this phosphate of alumina a value intermediate between that of scoria and that of the natural phosphates.—*La Chimica Industriale*, Jan., 1900.

THE CHEMICAL ACTION OF LIQUID SULPHUROUS ACID ON IRON.

By A. LANGE.

I HAVE already dealt with this subject in the *Zeitschrift für Angewandte Chemie*, and at the end of the article I emphasized the fact that the attacking of the iron by sulphurous acid would be particularly objectionable in the case of ice-making machines, and the necessity of keeping the acid absolutely anhydrous. As far as I am aware no importance has been attached, up to the present, to the proportion of water in the sulphurous acid used, either because the objections to it were not known, or because, in face of the present state of our knowledge, it was not easy to admit that sulphurous acid was capable of dissolving water. Now, water gets into the machine while at work, the more easily when there may be accidental falls of pressure in the compressor, exactly as has been shown with machines using ammonia, but no general explanation, covering all cases, has been given. But the moment the sulphurous acid circulating in the machine contains water, the attack of the iron should take place as I have observed, and this is helped by the high temperature of the compressor, if the action is not

prevented by other causes. I believe I have found one cause in the cooling generally applied to ice-making machines, using sulphurous acid, and especially in the neighbourhood of the cylinder and the piston. It must be admitted, and I have insisted on this point in the *Zeitschrift für die ges. Kälteindustrie* (May, 1899), that the sole object of the cooling is to keep these parts at a lower temperature than that at which the attack might take place with a somewhat impure sulphurous acid. It is always the cocks of the compressors, which cannot be protected in this manner, that should show traces of the attack by the action of aqueous sulphurous acid; still, as far as I am aware, such action has not been observed. Now, a little while ago, I received some material taken out of the compressor of a sulphurous acid machine, one which certainly had not been taken very much care of; I was asked, at the same time, if this substance would help me to explain how the corrosion took place. The material was black and friable, and lost 3 per cent of its weight in the desiccator and 14 per cent at 100°. By extraction it gave 15 per cent of an easily solidified fat. The solution obtained by treating the residue with cold water and filtering was neutralised with hydrochloric acid, and submitted to prolonged boiling. I thus obtained a precipitate coloured black by sulphide of copper. The solution thus contained copper. I easily obtained the reactions I have already described showing the presence of sulphurous and hyposulphurous acids and protoxide of iron. The substance further contained a large proportion of graphite, which is apparently due, like the fat extracted from the lubricating material, to the material used for making the cocks and pistons air-tight; a small proportion of it may also be due to the attack of the iron.

The presence of hyposulphite of protoxide of iron in the products of the corrosion establishes, in a decided manner, the fact that this latter is caused by the chemical action of the sulphurous acid on the iron, and that it is not the result of a mechanical action.

It was also evident, according to my experiments, that the attack took place owing to the presence of water in the acid; it was, however, important to determine this factor for the acid in the machine. The engineer having told me that water was frequently drawn off from the machine, I was led to admit that the acid was saturated with water, a saturation which my experiments showed to be 1 per cent.

However, one sample gave 0.2 per cent, and another, taken some days later—0.45 per cent of water; now the sample taken in both cases were not very good ones, and these figures it should be admitted are rather too high than too low. As the samples were brought in open vessels from the machine, a part of the sulphurous acid would escape in vapour, and thus cool the remainder below its boiling-point at the atmospheric pressure. Although we have not, as in the case of ammonia, made comparative experiments on the variations which may take place under these conditions, we are bound to admit that it is the pure acid which escapes, and then we should find in the remaining acid a proportion of impurities rather too high than too low. The samples obtained were cooled considerably; under these conditions the first became cloudy, with a deposit of small oily drops; on the surface of the second, small crystals appeared, probably a hydrate of sulphurous acid. The cooled samples were transferred to pipettes with taps, which had previously been exhausted of air, so that there was nothing to fear with regard to variation in composition. I must here draw attention to a phenomenon which occurred during the course of these researches, as well as in my previous research, either with pure sulphurous acid or with the acid diluted with water, and which I have not yet mentioned. If we allow the sulphurous acid to run out of the pipette extremely slowly, no change is observed in the acid remaining liquid; but if we open the tap in such a manner that there is a rapid volatilisation, so that the outside becomes covered with dew, the liquid becomes

cloudy, and thus crystalline deposits form round the sides of the vessel: these cakes always form a little above the surface of the liquid, and gelatinous or crystalline fragments break off and fall into the liquid, and float therein. When once the whole of the acid is distilled, and the pipette become warm, nothing but oily drops remain round the sides. These crystallisations are probably due to dissolved fat, and to the formation of hydrates of sulphurous acid. Now, how does it happen that, under these circumstances, a relatively great degree of purity of the sulphurous acid was noticed at the time of taking the sample, while the machine certainly contained strongly aqueous acid, and that seeing the amount of the product of corrosion for a considerable time? We may give the following answer to this question, an answer which will also explain why the action I suspected and observed either did not take place or did so only by accident, if the machine was working properly. By the cooling of the hot compressed gas leaving the compressor, there condenses in the upper part of the refrigerator (condenser), at the same time as the warm liquid sulphurous acid, the water eventually found. Now, as the warm, liquid, sulphurous acid is not able to dissolve so much water as the liquid acid at 15°, and that, further, the specific weight of the acid is to that of the water as 3 to 2 (about), the water remains in the upper part. Besides this, the fresh quantities of acid coming from the compressor are cooled in the same manner, and the condenser—serving also as a reservoir—remains always filled up to a certain height; in this way the water always remains above the reserve of acid which gradually descends, and it is only after having been thus purified that it is again cooled in the condenser without having had the opportunity of becoming saturated with water. As it is from the lower part that the acid is again taken to be volatilised, and then sent on to the compressor, the aspirated acid is always relatively pure. The condenser of the sulphurous acid machine thus acts as a sort of purifier; it is only necessary to be able, from time to time, to get rid of the water which accumulates. On the other hand, all this will only take place when the apparatus is well filled; if the machine contains too little sulphurous acid, the separation will certainly take place in the condenser, but the water will be re-aspirated at the same time as the acid, and the corrosion of the iron will be effected very easily, especially if the compression takes place at a temperature above 70°.

M. Harpf, in No. 21 of the *Zeitschrift für Angewandte Chemie*, has criticised my communication and rectified a small error which had accidentally crept in. He also draws attention to the equation I gave to explain the phenomenon of the solution of the iron in sulphurous acid containing water:— $2\text{Fe} + 3\text{SO}_2 = \text{FeSO}_3 + \text{FeS}_2\text{O}_3$.

It is evident that Schützenberger's explanation, that ferrous hydrosulphite is first formed and then turns into hyposulphite, is true in the case of the attack with commercial acid, since he recognises the necessity of water for the reaction which takes place. I have never been able to detect hydrosulphurous acid, but it must be remembered that this acid decomposes by heat, and my experiments have only been carried out at a fairly high temperature. The hypothetical hydrosulphite of iron is in any case decomposed before the cylinder is emptied and re-heated, but it is necessary during the experiment at a temperature higher than 70° that it be formed and decomposed into hyposulphite at the same time. Even in the product of the reaction, taken from the ice machine above mentioned, there was no hydrosulphurous acid, although the substance had not been re-heated. Finally, the supposition that the yellow colour of the pure sulphurous acid first used is caused by the presence of hydrosulphurous acid, is not altogether legitimate. It is certainly not inadmissible that commercial sulphurous acid contains this material, but then the cylinders and receptacles would be attacked, even at a low temperature, and this fact would decidedly complicate the conditions of transport of the pure acid. I therefore think that,

considering we have not proved the existence of hydro-sulphurous acid in the sulphurous acid, it is preferable to attribute the accidental yellow colouration of the latter to the presence of lubricating oil.—*Zeitschrift für Angewandte Chemie*, 1899.

THE PRODUCTION OF IODISED POTASSIUM AND AMMONIUM CARNALLITES.

By A. DE SCHULTEN.

THESE carnallites are obtained if, in the preparation of the bromised carnallites already described (*Bull. Soc. Chim.*, 1897, [3], xvii., 166), we replace the bromides by equivalent quantities of iodides.

To prepare the iodised potassium carnallite, we abandon a mixture of a solution of 8 grms. of iodide of potassium and 200 grms. of the salt $\text{MgI}_2 + 6\text{H}_2\text{O}$, to slow evaporation in vacuo over sulphuric acid. The crystals, dried between blotting-paper, and left over sulphuric acid, gave on analysis the following figures, leading to the formula $\text{KI}, \text{MgI}_2 + 6\text{H}_2\text{O}$:—

	Found.	Calculated.
K	7'34	7'09
Mg	4'36	4'42
I	69'00	68'93
H ₂ O	19'43	19'56
	100'13	100'00

The water was estimated by calcining the material with a large excess of oxide of lead.

Iodised carnallite occurs in flat prisms, having, like the bromised carnallite, the facets p (001), and m (110). The angles are 90° or thereabouts. The crystals are very hygroscopic, so I have not been able to measure the angle accurately.

The density of the crystals is 2'547 at 15°. Their molecular volume is therefore 217.

The iodised ammonium carnallite is obtained by the evaporation, in vacuo over sulphuric acid, of a solution containing 15 grms. of iodide of ammonium and 125 grms. of the salt $\text{MgI}_2 + 6\text{H}_2\text{O}$. The analysis of the crystals gave the following figures, leading to the formula $\text{NH}_4\text{I}, \text{MgI}_2 + 6\text{H}_2\text{O}$:—

	Found.	Calculated.
NH ₄	3'39	3'40
Mg	4'64	4'59
I	71'46	71'67
H ₂ O	20'19	20'34
	99'68	100'00

The water was determined in the same manner as with the corresponding bromised compound (*loc. cit.*).

The appearance and crystallographic properties of iodised ammonium carnallite are the same as those I have described for the iodised potassium carnallite. The crystals are very hygroscopic.

The density of the crystals is 2'346 at 15°. Their molecular volume is therefore 226.—*Bull. Soc. Chim.*, Series 3, xxxiii., No. 5.

The Hydrates of Chloride of Magnesium.—A. Bogorodsky.—The author confirms the existence of the hydrate with $12\text{H}_2\text{O}$ announced by van't Hoff and Meyerhoffer, and describes its interesting properties. A solution containing $\text{MgCl}_2 + 12\cdot06\text{H}_2\text{O}$ cooled down to -17° rapidly gives very beautiful crystals of the hydrate, which appear to be quadratic. They are lighter than the liquor in which they form. The crystallisation takes place with augmentation of volume, and is in every respect comparable to the congelation of water. The fusing point of this hydrate is -16°.—*Journ. Soc. Phys. Chim. R.*, xxx., 7, 735.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, April 27th, 1900.

Mr. T. H. BLAKESLEY, Vice-President, in the Chair.

THIS meeting, by invitation of Sir Norman Lockyer, F.R.S., was held in the Solar Physics Observatory, South Kensington.

Sir NORMAN LOCKYER gave "*A Short Account of the Physical Problems now being Investigated at the Solar Physics Observatory and their Astronomical Applications.*"

The chief work carried on at the Observatory is the comparison of stellar spectra with spectra obtained from lights emitted by laboratory sources. The light from a star (or the sun), and from an arc (or a spark), are focussed alternately upon the slit of a spectroscopic, and the two spectra are photographed side by side upon the same plate. The number of lines in the arc spectrum depends upon which part of the arc is focussed on the slit. The image of the centre is rich in lines, the image of the edge gives a few single lines. Changes in spectra are also dealt with. The thickening and thinning of lines depends upon several things. In the first place, it depends upon the density of the substance, and thus the hydrogen lines in the spectrum of Sirius are much broader than those in α Cygni, the hydrogen being denser in the former star. Changes may also be produced by variations in quantity. A reduction in the quantity of a substance generally simplifies its spectrum, the longest line disappearing last. The motion of a luminous body to or from the spectroscopic alters the wave-length of the light emitted, and produces a shift in the lines of the spectrum. The amount of deviation is a measure of the velocity of approach. In the case of Nova Aurigæ we have dark and bright lines of the same substance side by side. This shows that there are two bodies involved, moving with different velocities, the one giving a radiation, and the other an absorption spectrum. Another change in the lines depends upon temperature. In general, an increase in temperature produces a greater number of lines, a notable exception being sodium, which gives its full number of lines at the temperature of an ordinary Bunsen flame. The spectra of metals obtained from the arc and by sparking are often quite different. Those lines which make their appearance or are intensified in passing from the arc to the higher temperature of the spark are known as enhanced lines. The comparison of stellar spectra with laboratory spectra is often easy. For instance, the presence of iron in the sun, and hydrogen in Sirius is easily seen. Several lines in the spectrum of Bellatrix have been shown to be due to helium, the position of the lines being exactly the same as those due to the gases from cleveite. In many cases it is possible to build up the spectrum of a star from the spectra of its constituents taken at the proper temperatures. For instance, the spectrum of γ Orionis can be closely imitated by means of oxygen, nitrogen, and carbon, together with the well-marked lines of hydrogen and helium. We can roughly estimate by the character of the spectra of stars, the temperature of those stars, and thus arrive at a stellar thermometry. Starting with a hot star like Bellatrix, and passing through β Persei, γ Lyrae, Sirius, Castor, Procyon, to Arcturus, a cold star, we have a gradual change in the character of the lines which appear in the spectrum of any constituent. The widening of the lines in the case of spectra of sun-spots enables us to trace changes in temperature of the sun, and we can compare these temperature changes with a variety of terrestrial phenomena, such as variation in latitude. The extraordinary number of lines exhibited by many metals suggests that what we are accustomed to call chemical elements are really complex bodies, which are made up of simpler ones. Attempts

have been made to build up the spectra of metals by superimposing simple sets of lines upon one another. In many cases a great number of series would be required to represent things completely. In the case of hydrogen it would be necessary to have at least 27 series to give the structure spectrum only. Taking the atomic weight of hydrogen as unity the atomic weight of the little masses, which might give rise to any one of the series, would be about 0.0019. This is of the order of magnitude of the small bodies whose existence has been suggested by Professor J. J. Thomson from his work on ions.

NOTICES OF BOOKS.

A Manual of Chemistry, Inorganic and Organic, with an Introduction to the Study of Chemistry. By A. P. LUFF, M.D., B.Sc., F.I.C., and F. J. M. PAGE, B.Sc., F.I.C., &c. Illustrated with 40 Engravings. London: Paris, New York, and Melbourne: Cassell and Co., Lim. 1900. Pp. 541.

ALTHOUGH not so announced on the title-page, we find that this book is intended principally as a guide to the study of chemistry for the use of medical students. There is no doubt that chemistry and medicine are becoming more closely allied every year, and the physician is becoming more and more dependent on the chemist (not the druggist), especially in the matter of new organic compounds, the uses of which are so rapidly spreading in medicine.

Organic chemistry having become so vast a science, the student of medicine is apt, on the one hand, to find himself out of his depth, so to speak, in attempting to master the contents of the larger handbooks on the subject, while, on the other hand, many of the smaller works omit a good deal of matter which is essential to his ultimate success in medicine. It is to correct these two extremes that the authors have compiled this volume, bearing constantly in mind the special wants of the medical student, while at the same time ensuring to the careful reader a thorough grounding in the fundamental principles of modern chemical science.

Curiosities of Light and Sight. By SHELFORD BIDWELL, M.A., LL.B., F.R.S. With fifty illustrations. London: Swan, Sonnenschein, and Co., Limited. 1899. Pp. 226.

THE essays and lecture-notes which form the ground-work of this volume treat the subject in a popular and informal manner, which makes very pleasant reading. There is in fact no other easily accessible account of many of the curious matters touched upon. A perusal of this volume shows either what a very imperfect organ the human eye is, or else what very bad use we make of it. There is no wonder that the conjurer can make us see what he wishes us to see, when we find our eyes so easily deceived by straightforward experiments in which no deception is attempted or intended.

The author begins with an examination of the theory of light and its action on the eye. The essential nature of the action exerted by ether waves is still undetermined, though the old belief that the sensation was produced by a series of mechanical beats similar to the action of air-waves on the ear no longer carries any weight. Ether waves can bring about chemical changes as in photography; they can also produce electrical effects as, for example, when they are allowed to fall on a piece of prepared selenium; but it is inconceivable, and, further, there is no evidence that they are able to impart their own vibrations of such enormous frequency to any part of the human organism; many guesses at the truth have been made, but it is most likely that the effect is both electrical and chemical.

Again, the range of sensibility of different eyes may vary in the same manner as do different ears, and it is by no means probable that all animals, and especially insects, have the same limits of vision as man; further, the same vibrations falling in different places will give very different results. A chemical action will be caused by the ray falling on the leaf of a plant, an electrical action if it falls on a selenium cell, and the sensation of light if it falls on an eye.

In the portion of the book dealing with colour and its perception a great deal of interesting and little known information is to be found; while the chapters on optical illusions and curiosities of vision are most attractive, and will be read with enjoyment.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 24.

Binoxide of Molybdenum.—M. Guichard.—Already inserted.

Estimation of Sulphuric Acid in the presence of Iron.—G. Wyruboff.—A controversial paper, not suitable for abstraction.

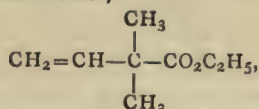
Antimonie Acids and Antimoniates.—A. E. Delacroix.—Already inserted.

Action of Sulphate of Methylene on Benzylic Alcohol.—Marcel Delépine.—For the safe utilisation of the action of sulphate of methylene on benzylic alcohol with the object of preparing the formol and the acid sulphuric ether of this alcohol, it is necessary to strictly adhere to the following rules:—The sulphate must be mixed with five or six parts of benzylic alcohol and slowly heated to 60–65° with continuous stirring. The temperature must not be allowed to surpass 70°, or the reaction will be so violent that the benzylic alcohol will instantly become resinous, and the temperature rise to over 300°. When all the sulphate is dissolved at the lower temperature, a pale yellow liquid results; agitation with water removes the greater part, but not the whole, of the acids formed. The acid liquors, neutralised with carbonate of barium, give dissolved benzylsulphate of barium. The still acid insoluble portion must not be distilled directly, for, at a certain moment, a violent reaction occurs, which carbonises everything, and the temperature rises to over 360°. To prevent this, the insoluble oil must be diluted with one volume of ether and neutralised with carbonate of potassium; a precipitate of bicarbonate, sulphate, and benzylsulphate of potassium is formed, from which the latter is extracted with boiling absolute alcohol. As for the ethereal solution, it is distilled *in vacuo* and fractionated; the benzylic alcohol passes over first, then the benzylic formol. Benzylic formol, $\text{CH}_2(\text{OC}_6\text{H}_5)_2$, is a colourless liquid, which does not solidify at –23°; it boils at about 210–220° under 20 m.m., and at 330° at the ordinary pressure. By evaporating the solution of benzylsulphate of barium *in vacuo*, it separates in long colourless needles having the formula $(\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$. Benzylsulphate of potassium crystallises in absolute alcohol in fine pearly needles; its proportion of potassium gives the anhydrous salt the formula $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{O}\cdot\text{SO}_3\text{K}$.

Preparation of Azelaic Acid.—M. Maquenne.—Castor oil is saponified by heating for a few minutes with an alcoholic solution of potash and diluting with warm water; the fatty acids are precipitated with a slight excess of sulphuric acid, decanted, washed, and dried. 30 grms. of the raw ricinoleic acid thus obtained are dissolved

in 200 c.c. of a 4 per cent solution of potash and gently heated, then poured suddenly into a 2-litre flask containing 1 litre of warm water (at about 35°) and 75 grms. of permanganate of potassium. When all the permanganate is dissolved, the flask is heated on the water-bath at 90° until the red colour entirely disappears, when 90 grms. of 50 per cent sulphuric acid are gradually added. The precipitate is filtered and washed with warm water; all the liquors are collected and made up to about 500 c.c. On cooling, the azelaic acid crystallises out in transparent flakes.

On α -Dimethylisocrotonic Acid (α -Dimethylbutinoic-3).—L. Bouveault.—The ethers of the non-saturated $\alpha\beta$ -acids condense easily with the soda derivatives of the malonate or the acetylacetate of ethyl. The author has tried whether the ethers of the non-saturated $\beta\gamma$ -acids have the same property. He therefore tried α -dimethylisocrotonic ether,—



prepared by the dehydration of the ether-alcohol. It was expected that the reaction would lead to α -dimethyladipic acid, or to an $\alpha\alpha\beta$ -trimethyl glutaric acid; there was, however, no condensation produced at all. It therefore seems that, for this interesting reaction to take place, the double bonds should be immediately adjoining a negative group. Some interesting results were, however, obtained, such as the preparation of the dimethyl- β -oxybutyrate of ethyl.

Rhamninase and Xanthorhamnine.—C. and G. Tanret.—For examining the activity of rhamninase, the authors prepared solutions of xanthorhamnine (at one-fiftieth), and added equal weights of rhamninase; that is, 0.165 gm. per 100 c.c. of solution containing 6.66 grms. of glucoside. After four hours and ten minutes in the oven at the desired temperature, the precipitates were collected, washed, and dried at 100°. The results obtained are given in the following table. T = the temperature of the experiment; t, the time when the precipitates commenced to deposit; P, the weights of these precipitates; and p, these weights in proportion to that formed at 70°, which was taken as 100.

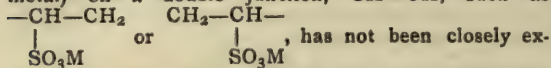
T.	t.	P.	p.
	Minutes.	Grms.	
85°	0	0	0
80	28	0.498	31.5
75	6	1.245	78.8
70	7	1.580	100.0
65	10	1.427	90.3
60	20	1.321	83.6
55	25	1.202	76.1
50	33	1.183	74.8
45	35	1.173	74.2
40	38	0.629	39.8
35	40	0.466	29.5
30	40	0.396	25.0
25	72	0.200	12.6
20	225	P too slight to collect.	

Saponification of Benzonitrile.—Ch. Rabaut.—By heating an alcoholic solution of benzonitrile with weak potash in a flask fitted with a vertical condenser, the author obtained benzamide in almost theoretical quantity. The return of benzamide is, in fact, a function of the quantity of potash used. If concentrated potash is used, benzoic acid is almost uniquely obtained. Under the same conditions, in the presence of potash, cyanide of benzyl gave the corresponding amide, but in less proportion.

Preparation of Anisic Aldehyde.—H. Labbé.—One part of anethol is added to 2 parts of glacial acetic acid in a large flask, and 3½ parts of nitric acid at 14 B. are

run in, taking care to put a few fragments of pumice at the bottom of the flask. The flask must be gently heated and shaken from time to time. After the oxidation is completed (about half an hour), the insoluble part is separated by decantation by means of a stoppered funnel, the aqueous portion is saturated with carbonate of soda; this separates an oil which is added to the first. This oil is agitated with bisulphite of soda; the crystallised magma, dried by means of a filter-pump, is washed with alcohol and ether. The preparation is then finished in the ordinary way. The return by this method is 69 or 70 per cent of theory.

Fixation of Acid Sulphite of Sodium on Double Junctions.—H. Labbé.—The fixation of a radical SO_3MH (M being an alkaline or alkaline-earth metal) on a double junction, $\text{CH}=\text{CH}$, such as



has not been closely examined up to the present. The author has undertaken the examination of the subject with regard to different characteristic functions and different classes of compounds (aliphatic, aromatic, or terpenic). His first experiments have largely confirmed the hypothesis that the characteristic function of the molecule should have an influence on the greater or less facility with which double junctions of the molecule fix the acid sulphitic radical; while later experiments show that the phenomenon is governed by three principal factors—the nature of the compound, its characteristic function, and its solubility in the aqueous medium.

Genesis of the Terpenic Constituents of Essence of Bergamot.—C Charabot.—The author finds that during the maturing of the fruit of the *Citrus bergamia*, the composition of the essential oil is modified in the following manner:—1. The proportion of the free acids diminishes slightly. 2. The richness in acetate of linalyl increases. 3. The proportion of free linalol, and even of total linalol, diminishes in a very marked manner. 4. The quantity of the terpenes augments, without the relative proportion of the two carbides being modified. 5. The proportion of bergaptene diminishes. To sum up, the active period of the formation of the linalol is that corresponding with the development of the fruit, the etherification accompanied by dehydration of this terpenic alcohol takes place mainly during the maturing of the fruit.

MISCELLANEOUS.

Royal Institution.—The Annual Meeting of the Members of the Royal Institution was held on May 1st; Sir J. Crichton-Browne in the Chair. The Annual Report of the Committee of Visitors for the year 1899, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read. Sixty-three new Members were elected in 1899. Sixty Lectures, Seventeen Evening Discourses, and two Centenary Commemoration Lectures were delivered in 1899. The Books and Pamphlets presented in 1899 amounted to about 280 volumes, making, with 672 volumes (including Periodicals bound) purchased by the Managers, a total of 952 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committee of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—President—The Duke of Northumberland; Treasurer—Sir James Crichton-Browne; Secretary—Sir William Crookes; Managers—Sir Fred-

erick Abel, Bart., Sir Frederick Bramwell, Bart., Dr. Thomas Buzzard, Sir William James Farrer, Mr. Hugh Leonard, The Right Hon. Lord Lister, Mr. Frank McClean, Mr. Raphael Meldola, Dr. Ludwig Mond, Sir Andrew Noble, Mr. Alexander Siemens, Mr. Basil Woodd Smith, Mr. William Hugh Spottiswoode, The Hon. Sir James Stirling, and Sir Henry Thompson, Bart.; Visitors—Dr. Charles Edward Beevor, Mr. William Henry Bennett, Mr. W. A. B. Burdett-Coutts, Mr. Joseph G. Gordon, Mr. Maures Horner, Sir Alexander Campbell Mackenzie, Mr. Henry Francis Makins, Mr. Carl Edward Melchers, Mr. John Callander Ross, Mr. William James Russell, Mr. Alan A. Campbell Swinton, Sir James Vaughan, Mr. John Jewell Vezey, Colonel H. Watkin, and Mr. James Wimshurst.

A Hydrated Bromide of Copper and Lithium.—N. Kournakoff and A. Sementchenko.—By evaporating on the water-bath a solution of CuBr_2 and 2BrLi until the appearance of crystals, and then allowing to cool while protected from moisture, we obtain black needles, appearing bronze by reflected light, excessively hygroscopic, having the formula $\text{CuBr}_{2.2}(\text{LiBr}_3\text{H}_2\text{O})$. The authors admit that the water of crystallisation is fixed to the lithic and not the cupric salt.—*Journ. Soc. Phys. Chim. R.*, xxx, 701.

MEETINGS FOR THE WEEK.

- MONDAY, 7th.**—Society of Arts, 8. (Cantor Lectures). "The Incandescent Gas Mantle and its Use," by Prof. Vivian B. Lewes.
— Royal Institution, 5. General Monthly Meeting.
- TUESDAY, 8th.**—Royal Institution, 3. "Studies in British Geography," by Hugh Robert Mill, D.Sc., LL.D., &c.
— Society of Arts, 8. "Art Metal Work," by Nelson Dawson.
- WEDNESDAY, 9th.**—Society of Arts, 8. "Improvement of our Roads," by A. Moresby White.
— Royal. (Conversazione).
— and THURSDAY, 10th.—Iron and Steel Institute, 10.30. Annual Meeting.
- THURSDAY, 10th.**—Royal Institution, 3. "A Century of Chemistry in the Royal Institution," by Prof. Dewar, M.A., LL.D., F.R.S.
- FRIDAY, 11th.**—Royal Institution, 9. "Shakespeare and True Patriotism," by Sidney Lee.
— Physical, 5. Discussion of Prof. Lodge's Paper "On the Controversy concerning Volta's Contact Force." "Heat of Formation of Alloys," by J. B. Taylor. "Want of Uniformity in the Action of Copper-Zinc Alloys on Nitric Acid," by Dr. Gladstone, F.R.S. An Electromagnetic Experiment, and Experiments illustrating the Aberration called Coma, by Prof. S. P. Thompson, F.R.S.
- SATURDAY, 12th.**—Royal Institution, 3. "South Africa—Past and Future," by Dr. Alfred P. Hillier.

Assistantship required. Works experience and also with leading Public Analyst. Highest references.—B., 21, Groombridge Road, Hackney, London, N.E.

A thoroughly qualified Chemist (F.I.C.) desires an appointment as Chemist or Manager in Works or Laboratory. Many years' experience in important works and in Bacteriology. Highest references. No objection to going abroad.—Address, F.I.C., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

A Young Chemist, with training in Technical Institute and Analyst's Laboratory, seeks Employment as Junior Assistant. Experience in Agricultural Products, Manures, &c., and Qualitative and Quantitative Analysis. Excellent testimonials.—Address, "Chemist," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, a Position in a Public Analyst's Laboratory as Assistant. Several years' experience in Water, Food, Drugs, Bacteria, and Assaying. Good testimonials. Aged 22.—Address, M. L., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, a superior Process for producing VENETIAN RED FROM SULPHATE OF IRON (GREEN VITRIOL). Only such persons need apply who are able to supply samples and give exact figures about consumption of fuel in the furnace, as economy in coal is the principal point.—Address, Henrik Weit, Warsaw (Poland).

THE CHEMICAL NEWS.

VOL. LXXXI., No. 2111.

THE KINETIC THEORY OF PLANETARY ATMOSPHERES.*

By G. H. BRYAN, Sc.D., F.R.S.

THE application of the kinetic theory to the atmospheres of planets dates from the paper of Waterston, who gave an investigation based on the then only possible assumption of equal velocities for all molecules, an assumption since known as Clausius's law. Of later papers reference is due in especial to Dr. Johnstone Stoney's memoir "Of Atmospheres on Planets and Satellites" (*Trans. R. Dublin Soc.*), in which the test of permanence of a gas in the atmosphere of a planet is made to depend on the ratio of its velocity of mean square to that relative velocity which would enable a suitably projected body to escape from the planet's attraction. If it be admitted, as Dr. Stoney assumes, that helium cannot exist in our atmosphere, it follows that vapour of water cannot exist on Mars.

The author's object has been to investigate the logical conclusions obtained by applying the Boltzmann Maxwell distribution to the atmospheres of planets. In 1893 calculations were made, having special reference to the absence of atmosphere from the Moon, but these took no account of axial rotation. When this cause is taken into account, the distribution of co-ordinates and relative velocities of the molecules is found to be the same as if the planet were at rest, and "centrifugal force" applied to the system. The surfaces of equal density are of the forms originally investigated by Edward Roche, of Montpellier, and they cease to be closed surfaces when passing to the outside of the point on the equatorial plane where centrifugal force just balances the planet's attraction. Calling the surface through this point the "critical surface," the density of molecular distribution over this surface must be very small to ensure permanence. The ratio of the density at the planet's surface to the density at the critical surface has been called the "critical density ratio," and the author calculates its logarithm for particular gases at different temperatures on the various planets. The use of this logarithm has the advantage that the calculation can at once be extended to any gas at any temperature.

The high value obtained in the case of helium considered in reference to the earth, appears to afford abundant proof that if helium existed in our atmosphere it would possess a very high degree of permanence at ordinary temperatures. To test this point further, a calculation is made of the total rate at which molecules would flow across the critical surface, this rate being regarded as a superior limit to the rate at which the planet would lose its atmosphere, since it takes no account of molecules which describe free paths beyond the limit and fall back again. To further exhibit the results in a tangible form, the rate of flow is estimated by the number of years in which the total amount of gas escaping across the critical surface would be equal to the amount of the gas in a layer covering the surface of the planet to the depth of 1 c.m. This measure is independent of the actual quantity of the gas under consideration existing in the atmosphere, since, if this quantity be increased, the rate of flow across the critical surface and the amount of gas present in the surface layer 1 c.m. thick will be increased in the same proportion.

If a gas of molecular weight 2, such as helium, be supposed to exist in the earth's atmosphere, the loss in

question would occupy 3.5×10^{10} years at -73°C. , 3×10^{11} years at 27°C. , 8.4×10^{10} years at 127°C. , 6×10^8 years at 227°C. , and 222 years at 327°C.

If we halve the absolute temperatures we have the conditions applicable to hydrogen, the losses in question therefore taking place in 8.4×10^{10} years at -73°C. , 6×10^8 years at -23°C. , and 222 years at 27°C.

For water vapour on Mars, the corresponding results are 1.2×10^{11} years at -73° , 1.9×10^{10} years at 27° , 2.4×10^9 years at 127° , 4.3×10^8 years at 227° , and 106 years at 327° .

These figures indicate that helium cannot practically escape from our atmosphere at existing temperatures, nor can vapour of water escape from the atmosphere of Mars. A leakage may and undoubtedly does take place which may appear considerable when estimated by the number of actual molecules escaping, but it is wholly inappreciable relative to the mass of gas left behind.

At a future time I propose to examine the corresponding results, based on the hypothesis that the atmosphere of a planet is distributed according to the adiabatic instead of the isothermal law.

ON THE DISCOVERY AND OCCURRENCE OF MINERALS CONTAINING RARE ELEMENTS.*

By Baron A. E. NORDENSKIÖLD.

THE first mineral referred to is scheelite, and the next cerite, which contains no less than four rare metals. The incandescent light produced when the latter mineral is fused with charcoal powder was first observed by Cronstedt in 1751. The discovery of glucina, lithia, selenium, and yttria is next referred to. Minerals containing yttria and oxides related to it were, at one time, thought to be almost limited to certain pegmatite-veins running in a broad zone on both sides of the 60th parallel of latitude. Latterly, fluocerite, orthite, and gadolinite have been found in Dalecarlia; and among these minerals Benedicks discovered a silicate of yttrium containing 1.5 per cent of nitrogen and helium. The author discovered kainosite, a silico-carbonate of yttrium and calcium, among minerals from Hitterö; and the same mineral was subsequently discovered in the flucan, fissures, and drusy cavities at the Nordmarken mines. The last mentioned discovery and others related to it appear to suggest that the mode of formation of fissure-minerals is not so unlike that of the pegmatite-veins of the Primary rocks as is generally supposed.

Thorium, discovered by Berzelius in 1829, was originally obtained from the rich mineral-locality of Langesund (called Brevig in mineralogical literature), but it has since been recorded from other localities, including Arendal and Finnish Lapland. It is now obtained from the monazite-sand of rivers in the Brazils and South Carolina. Thorite contains about 0.5 per cent of inactive gas, probably a mixture of nitrogen and helium; but the latter element was first obtained from the mineral cleveite, also containing thorium, discovered by the author in 1877. Other minerals bearing nitrogen, argon, or helium are referred to; and under the head of minerals bearing tantalum, mention is made of Giesecke's discoveries in Greenland. Among these is fergusonite, one of the richest sources hitherto known for obtaining that mysterious gas, or mixture of gases, which on our planet seems to be almost exclusively confined to minerals containing rare earths. "The group of earths, as well as the group of gases, of which we are here speaking, might therefore be compared with certain genera among organic beings, whose species, having not yet fully differentiated, offer to the descriptive zoologist or botanist difficulties analogous to those with which chemists meet in endeavouring to separate the rare earths and rare gases."

* Abstract of a Paper read before the Royal Society, April 5, 1900.

* Read before the Geological Society of London, April 4th, 1900.

DISCUSSION.

Prof. MIERS remarked on the isolated occurrence of the rare elements in certain patches of the earth's surface, and deplored the ignorance which at present prevails concerning their distribution in Cornwall, where rhabdophane, churchite, and monazite have been discovered; monazite he had himself found in the slate at Tintagel. The interesting historical survey given in the present paper directed attention to the importance of the mineralogical distribution of these rare elements.

THE PREPARATION OF FLUORINE BY ELECTROLYSIS IN AN APPARATUS OF COPPER.

By HENRI MOISSAN.

UP to the present time fluorine has been obtained by the electrolysis of a hydrofluoric solution of fluoride of potassium in a platinum apparatus. Shortly after the commencement of our research we announced that the platinum of the electrodes and of the apparatus was attacked, that a certain quantity of this metal went into solution, and that from this moment the electrolysis became more regular (*Ann. Chim. Phys.*, [6], xxiv., p. 224).

The use of platinum, and the wearing of the electrodes and of the vessel, which was fairly rapid, made this apparatus very expensive.

To find out whether it was possible to replace the platinum by another metal we placed samples of various metallic wires at the bottom of the electrolytic apparatus and proceeded with the preparation of the fluorine in the usual manner. We observed that, of the different metals used in these experiments, the one that was attacked the least was copper, that is, if the acid was perfectly free from water. This fact further agrees very well with the researches made by M. Poulenc on the properties of fluoride of copper (*Ann. Chim. Phys.*, [7], xix., p. 66).

In view of these preliminary experiments we constructed a copper U-tube, of as near as possible the same shape as our platinum electrolyser. Its volume was a little greater, being of about 300 c.c. capacity, and easily permitting the electrolysis of 200 c.c. of hydrofluoric acid, made conducting by means of 60 grms. of hydrofluorate of fluoride of potassium. The method of closing the apparatus was the same, but the shape of the electrodes was changed. In our previous experiments we made use of cylindrical rods of platinum the ends of which were clubbed; wishing to have a greater surface we gave the electrodes the form of open hollow cylinders. The surface was increased so as to get a higher return. The electrodes were still of platinum, as for this part of the apparatus we were unable to use copper.

In some experiments made with copper electrodes the metal went into solution as soon as the electrolysis began, and a badly conducting layer of fluoride of copper, which stopped the current, was quickly deposited on the positive electrode. If the mixture of hydrofluoric acid and fluoride of potassium is entirely free from water, the electrolysis goes on very satisfactorily with platinum electrodes in a copper vessel. Under these conditions this latter will not be attacked; it is probable that the fluorine which soon goes into solution in the hydrofluoric acid forms on the surface of the copper a thin layer of this protecting fluoride, of which we have previously spoken, insoluble in hydrofluoric acid.

The return from this apparatus was found by measuring the volume of the hydrogen given off at the negative pole in a certain time. In a series of preliminary experiments we satisfied ourselves that the volume of oxygen produced by the action of the fluorine on the water corresponded with the volume of hydrogen given off at the positive pole, allowing, of course, for the amount of ozone formed.

With a current of 50 volts and 15 ampères we obtained a return of about 15 litres per hour when the experiment lasted about from six to ten minutes. By using a current of 20 ampères at the same voltage the return was increased to 8 litres, but in the second case the experiment could not be continued for long owing to the heating of the liquid, and, in spite of an artificial cooling of -50° , the fluorine gas carried off abundant fumes of hydrofluoric acid.

It is also of importance not to lower the temperature too much, or there will be a considerable formation of a compound of hydrofluoric acid with the alkaline fluoride. This new copper apparatus gave very good results in experiments lasting several hours, and we were able to examine several new questions, for which a continuous current of fluorine was necessary.—*Bull. Soc. Chim.*, Ser. 3, xxiii., No. 8.

RAPID METHOD FOR THE ESTIMATION OF CLAY IN SOILS.

By F. POQUILLON.

THE usual method adopted for making this estimation is a very tedious one; by its means we cannot estimate the clay in less than eight or ten days.

The method I am about to describe will enable this estimation to be done in two or three days at the most. It is based on the fact that if, instead of mixing the earth with distilled water, we use a dilute solution of hydrochlorate of ammonia, the clay is held in suspension while it is at the same time coagulated, thus enabling the sand to deposit almost immediately.

Ten grms. of the soil are placed in a small porcelain crucible and rubbed round the sides with the first finger while adding water, drop by drop, until about 25 c.c. has been added. This mixture is transferred to a beaker of 150 c.c. capacity, and about 100 to 120 c.c. of a solution of hydrochlorate of ammonia, at 1 gm. per litre, are added. After well stirring with a glass rod, it is allowed to settle for five minutes, and the liquid decanted into a 1 litre beaker. On this residue 100 to 125 c.c. more of the hydrochlorate solution are poured; stir well again, allow to stand for five minutes, and decant into the 1 litre beaker. This operation is repeated until the wash-waters are quite clear: this will require six or eight washings for the most argillaceous soils. The residue is treated with hydrochloric acid diluted with water, washed with distilled water, and dried; its weight gives the total sand.

The thick liquid remaining in the 1 litre beaker is treated with a few drops of hydrochloric acid, to decompose the calcareous matter and complete the coagulation of the clay. It is then allowed to stand until the supernatant liquid is clear; this requires two or three hours. The clay which deposits is collected on a weighed filter, washed with distilled water, dried, and weighed.

This method has the following advantages over the old one:—

1. Instead of making two washings on the filter, one to remove the lime and chalky matter and the other to free the clay from the hydrochlorate of ammonia, a single washing enables us to get rid of both the lime and hydrochlorate at the same time.
2. Instead of obtaining the clay in suspension in 4 or 5 litres of water, it is now found in 750 to 1000 c.c.: this is in one-fifth or in one-sixth of the volume.
3. Instead of getting the clay on the filter after five or six days, this stage is reached after about three hours.
4. The clay obtained by this process is washed more rapidly than that obtained by the old method (I have never taken more than a day and a half to effect the same amount of washing that used to require three or four days by the old method).

Finally, the result obtained by these two methods, used simultaneously, are absolutely comparable, as the following figures will show:—

Clay, per Thousand Parts of Soil.

Old method = 206.0, 60.2, 198.0, 218.0, 122.0, 129.3.

New method = 205.8, 60.5, 198.0, 217.1, 121.9, 129.5.

—Bull. Soc. Chim., Series 3, vol. xxiii., No. 4.

THE PRODUCTION OF VANADINITES OF CADMIUM.

By A. DE SCHULTEN.

In a paper on the phosphates and arseniates of cadmium (Bull. Soc. Chim., Series 3, vol. i., p. 472) I showed that this metal forms apatites and arsenio-apatites. That being so, I tried whether cadmium would also form vanadinites, and I obtained, as result, a chlorovanadate and a bromovanadate of cadmium belonging to the family of vanadinites.

Chlorised Vanadinite of Cadmium.—To prepare this body we melt 50 grms. of chloride of cadmium with 4 grms. of carbonate of cadmium and 1.4 grms. of vanadic anhydride. On cooling the melted mass, very fine needles of vanadinite of cadmium are formed, which are separated by washing with water. By diminishing the quantity of chloride of cadmium in this experiment, we can get a slightly more voluminous crop of crystals, but they are contaminated with impurities. These crystals can be purified by treating them with dilute acetic acid. But the crystals will, in any case, be slightly attacked by this treatment. The analysis of these crystals gives the following figures, which lead to the formula $3\text{Cd}_3(\text{VO}_4)_2\cdot\text{CdCl}_2$:—

	Found.	Calculated.
Cl	3.69	3.76
Cd	59.95	59.51
V ₂ O ₅	29.01	29.08
O	7.35 (by diff.)	7.65
	100.00	100.00

The crystals dissolve easily in weak acids. When heated to redness they melt, giving off fumes of chloride of cadmium. In the cooled mass prismatic crystals can be seen, which are probably regenerated vanadinite.

Chlorised vanadinite of cadmium occurs in long hexagonal prisms. They are negative, and their density is 5.264 at 15°.

Bromised Vanadinite of Cadmium.—This body is obtained if, during the preparation of chlorised vanadinite just described, we replace the chloride of cadmium by the same quantity of bromide of cadmium. Bromised vanadinite of cadmium crystallises more readily than the chlorised vanadinite. The analysis of the crystals gave the following results, leading to the formula $3\text{Cd}_3(\text{VO}_4)_2\cdot\text{CdBr}_2$:—

	Found.	Calculated.
Br	75.9	8.10
Cd	56.98	56.83
V ₂ O ₅	27.48	27.77
O	7.95 (by diff.)	7.30
	100.00	100.00

The chemical, crystallographical, and optical properties of bromised vanadinite of cadmium are the same as those described for the corresponding chlorised compound. Its density is 5.456 at 15°.

By fusing carbonate of cadmium and vanadic anhydride with a large excess of iodide of cadmium, I obtained a small quantity of crystals having the appearance of the above-described vanadinites. These crystals, which con-

tain iodine, vanadic acid, and cadmium, are probably iodised vanadinite of cadmium. However, I have not been able to remove the impurities present in these crystals without the latter being strongly attacked.—Bull. Soc. Chim., Series 3, vol. xxiii., No. 5.

THE MEASUREMENT OF LOW TEMPERATURES.

By A. LADENBURG and C. KRUEGEL.

The authors have made use of a platinum-rhodium thermo-electric couple, and took three fixed points, viz.—the boiling-point of liquid air, -187°; the boiling-point of ethylene, -102.65°; and the sublimation point of a mixture of carbonic anhydride and alcohol, -76.6°. The temperature, t , was given a function of the number x of millivolts, by the equation—

$$t = -24.948x + 1.6744x^2 - 0.2248x^3.$$

The correctness of this relation was controlled by taking the boiling-point of methane. The following results were obtained:—

	Boiling-point. °	Pressure. M.m.	Melting-point. °
Oxygen	-181.4	745	—
Nitric oxide	-141.4	757.2	-150
Ammonia	—	—	-77.05
Methane	-152.5	749	—
Ethane	-85.4	749	-171.4
Ethylene	-102.65	756.9	—
Propylene	-50.2	749	Remains liquid in liquid air.
Trimethylene	-35 about	749	-126
Acetylene	-83.8 subl.	—	—
Toluene	+110	—	-94.2
Ethylbenzene	+135-136	—	-94.2
Mesitylene	+164	—	-59.6
Cymene	—	—	-75.1
Chloride of methyl..	—	—	-103.6
Bromide of ethyl ..	—	—	-116
Methylic alcohol ..	—	—	-94.9
Ethylic alcohol ..	—	—	-112.3
Ether	—	—	-112.6
Aldehyde	—	—	-120.7
Acetone	—	—	-94.9
Glycol	—	—	-17.4
Formate of methyl..	+32-33	—	-101.3
Acetate of ethyl ..	—	—	-83.8
Ethylamine	+19-20	—	-85.2

Absolute alcohol, plunged into liquid air, congeals into an absolutely vitreous mass; if this is re-heated very slowly it forms a viscous substance, which if again cooled down slowly gives this time a crystalline opaque mass. Ether, acetone, and aldehyde crystallise directly.—Berichte, xxxii., p. 1818.

REDUCTION OF REFRACTORY METALLIC OXIDES BY ALUMINIUM.

By F. KUPPELWIESER.

In the accompanying table the author gives the results of his theoretical calculations relative to the possibility, from the thermo-chemical point of view, of applying Goldschmidt's process for the reduction of the metallic oxides by means of finely-divided aluminium (Moniteur Scientifique, March, 1899, p. 199). We thus see that the process is applicable in every case, with the exception of that of silica, where there is a deficit of 622 calories,

	For the production of 1 kilo. of—					
	Iron.	Manganese.		Silicon.	Chromium.	Tungsten.
Oxide used	Fe ₂ O ₃ .	MnO ₂ .	Mn ₂ O ₃ .	SiO ₂ .	Cr ₂ O ₃ .	WO ₃ .
Aluminium required kilos.	0.484	0.656	0.492	1.272	0.520	0.294
Heat developed calories	3459	4684	3512	9.82	3713	2099
Heat absorbed by reduction "	1796	2115	2000	7830	2200	1100
Heat for fusion of the slag "	548	742	550	1439	582	324
" " metal "	362	535	535	435	434	360
Total heat absorbed "	2706	3392	3090	9704	3216	1784
Difference (possibly from radiation or other losses) "	+750	+1299	+421	-622	+497	+315

In the experiments described by the author, the iron obtained was perfectly fluid, as was also the slag. The metal was sufficiently hot in itself to melt the submerged extremity of a bar of iron (10 m.m. diameter) in two minutes. It is, however, noteworthy that the metal thus obtained could not be worked hot, probably on account of the presence of dissolved oxygen. In the first experiment with manganese, pyrolusite was used; in the second, braunite. In both cases the metal obtained was perfectly fluid. According to Van der Welde, the fusing-point of manganese is 1900°; that of chromium is higher than that of platinum, and should be about 2200°.

The thermic data of tungsten are uncertain, and the margin of 315 calories is probably too small, since the reduction of tungstic acid was effected without difficulty. (*Österr. Zeit. Berg- und Hüttenwesen*, 1899, p. 147.)

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.*

By LILY G. KOLLOCK.†

INTRODUCTION.

THAT the electric current has greatly aided in the development of new and reliable methods for the determination and separation of metals is no longer questioned. That new material will continue to be added to what we now possess is also certain to occur. But in the old methods worked out long before correct ideas prevailed as to current density, concentration of the solution and electrode surface, gaps exist, and uncertainty must necessarily prevail in the minds of those who seek to reproduce the proper working conditions of these earlier methods. That the latter are in every sense satisfactory in the hands of those persons who are thoroughly acquainted with them is also beyond question. To render them, however, universally acceptable, and to render their place in analytical chemistry by electrolysis permanent, the absolute conditions for successful work on the part of any investigator must be definitely established. To this end, a number of the earlier methods in which the double cyanides were used as electrolytes have been carefully reviewed in the following pages, and the conditions of current density, ampérage, voltage, and other factors fully worked out. Thus edited, doubt can no longer be thrown upon the methods proposed, and they will continue to be in their developed condition the most reliable for the purposes for which they have been suggested. They now for accuracy, neatness, and rapidity of execution most certainly excel the ordinary gravimetric and volumetric methods applied to the same metals.

CADMIUM.

In 1878 Smith showed that cadmium could be precipitated quantitatively from its alkaline double cyanide solu-

tion. In the following experiments cadmium sulphate containing 0.1659 grm. cadmium in 10 c.c. was converted into the double cyanide, using 1 grm. of potassium cyanide. The solution was electrolysed with a current N.D.₁₀₀=0.04–0.06 A and V=2.9–3.2. The solution was heated to 60° C. After the current had passed for six hours, the deposit was washed with hot water and alcohol, dried, and then weighed. The solution poured out of the platinum dish, and examined qualitatively for cadmium, showed that all the cadmium had been deposited in this time. It was likewise entirely precipitated when the current was allowed to act on the solution through the night in the cold. The following results were obtained (see Table I.).

SILVER.

It is stated (Smith's "Electro-chemical Analysis," p. 77) that silver may be precipitated from a cyanide solution containing an excess of potassium cyanide. It may be deposited with a low current, and has the advantage of non-precipitation of silver peroxide at the anode.

Accordingly a silver nitrate solution containing 0.1270 grm. of silver in 25 c.c., after the addition of 0.5 grm. of potassium cyanide, was diluted to 125 c.c. This solution was electrolysed with a current N.D.₁₀₀=0.07 A and V=3.2. The temperature was 65° C. The deposition was complete in three hours. With a current of N.D.₁₀₀=0.1 A the silver was deposited completely in two hours. The relation between the current and the time factor may be seen in Table II.

Separations.

Silver from Platinum.—Smith (*Am. Chem. Journ.*, xiii., 417) described this separation. A current of 1 c.c. of oxy-hydrogen gas per minute acted upon a solution of the double cyanide produced by adding 2½ grms. of potassium cyanide. The silver was deposited free from any trace of platinum.

The separation, therefore, was taken up in order to get the exact working conditions. The salts of the metals used were silver nitrate containing 0.1026 grm. of silver, and platonic chloride containing from 0.0879 grm. to 0.1758 grm. of platinum. To the combined solutions 1.25 grms. of potassium cyanide were added, and the whole diluted to 125 c.c. The current used was N.D.₁₀₀=0.04 A and V=2.5. The temperature was 70°. In from three to four hours the current was interrupted, and the deposit washed with hot water and alcohol. It was found to be free from platinum. The filtrate gave no reaction for silver. (See Table III.).

Silver from Copper.—In the *American Chemical Journal* (xi., 264) there appears a series of forty experiments relating to the separation of these metals. Copper was found to have been precipitated with the silver when the deposition took place from a cyanide solution. It was then thought that copper could not be separated from silver by this method. In 1889 a set of new experiments was reported. By lowering the strength of the current the separation was made. The silver deposit contained no copper, nor could silver be detected in the copper solution poured from the dish. In 1895 Smith and Wallace published a report of the separation made in that year,

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xxi., No. 10.
† From the author's thesis for the degree of Ph.D.

TABLE I.

Cadmium. Grm.	Potassium cyanide. Grm.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time.	Metal found. Grm.
0.1659	1	125	N.D. ₁₀₀ = 0.06 A.	2.9	57°	7 hours	0.1657
0.1659	1	125	" = 0.04 A.	2.9	Cold	During night	0.1650
0.1659	1	125	" = 0.06 A.	3.2	60°	3 hours	0.1655

TABLE II.

Silver present. Grm.	Potassium cyanide. Grm.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.
0.1270	0.5	100	N.D. ₁₀₀ = 0.07 A.	3.2	65°	3	0.1271
0.1270	0.5	100	" = 0.07 A.	3.2	65°	3	0.1270
0.1270	0.5	100	" = 0.06 A.	3.2	65°	3	0.1273
0.1270	1	100	" = 0.01 A.	3	65°	2	0.1268
0.1026	1	100	" = 0.04 A.	2.5	65°	5	0.1026
0.1026	1	100	" = 0.04 A.	2.5	65°	5	0.1024

TABLE III.

Silver. Grm.	Platinum. Grm.	Potassium cyanide. Grm.	Current.	Voltage.	Temperature.	Dilution. C.c.	Time. Hours.	Found. Grm.
0.1026	0.879	0.5	N.D. ₁₀₀ = 0.05 A.	2.5	78°	125	5	0.1030
0.1026	0.1758	1.25	" = 0.05 A.	2.5	75°	125	3	0.1022
0.1026	0.1758	1.25	" = 0.45 A.	2.4	75°	125	3	0.1028
0.1026	0.1758	1.25	" = 0.04 A.	2.5	75°	125	3	0.1025
0.1026	0.1758	1.25	" = 0.04 A.	2.5	75°	125	3	0.1025

TABLE IV.

Silver. Grm.	Copper. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.
0.1024	0.0998	2	125	N.D. ₁₀₀ = 0.03 A.	1.16	Cold	10	0.1027
0.1024	0.1	2	125	" = 0.05 A.	1.1	65°	7	0.1026
0.1024	0.1	1	125	" = 0.058 A.	1.66	65°	3	0.1026

TABLE V.

Silver. Grm.	Cadmium. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.
0.1024	0.168	2	125	N.D. ₁₀₀ = 0.02 A.	2.15	75°	4	0.1025
0.1024	0.168	2	125	" = 0.02 A.	2.1	60°	4	0.1020
0.1024	0.168	2	125	" = 0.025 A.	2.15	65°	5	0.1027

TABLE VI.

Silver. Grm.	Zinc. Grm.	Potassium cyanide. Grm.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.
0.1024	0.1	1	100	N.D. ₁₀₀ = 0.33 A.	2.76	60°	3	0.1026
0.1024	0.1	1	100	" = 0.38 A.	2.73	70°	3	0.1028
0.1024	0.1	1	100	" = 0.38 A.	2.70	65°	3	0.1027

TABLE VII.

Silver. Grm.	Nickel. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.
0.1024	0.1	1.5	125	N.D. ₁₀₀ = 0.02 A.	1.7	65°	3	0.1026
0.1024	0.1	1.5	125	" = 0.03 A.	2	65°	5	0.1025
0.1024	0.1	1.5	125	" = 0.03 A.	1.66	60°	3	0.1025

TABLE VIII.

Silver. Grm.	Cobalt. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.
0.1024	0.1	2.75	125	N.D. ₁₀₀ = 0.038 A.	2.2	65°	5	0.1028
0.1024	0.1	3.5	125	" = 0.02 A.	2.2	65°	3½	0.1027

TABLE IX.

Silver. Grm.	Iron. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.
0.1002	0.1	3	125	N.D. ₁₀₀ = 0.025 A.	1.8	65°	4	0.1001
0.1002	0.1	2.5	125	" = 0.02 A.	1.8	70°	4	0.1005
0.1002	0.1	3.25	125	" = 0.038 A.	2.2	65°	3	0.1000
0.1174	0.1	3	125	" = 0.04 A.	2.25	70°	3	0.1176
0.1174	0.2	4	125	" = 0.04 A.	2.2	70°	3	0.1174
0.1174	0.1	3	125	" = 0.05 A.	2.2	75°	3	0.1175

I found that the following conditions gave accurate results. The solution of silver nitrate used contained 0.1024 grm. of metal and that of copper nitrate contained 0.0998 grm. of copper. To the mixed solution 2 grms. of potassium cyanide were added. The liquid containing an excess of potassium cyanide was diluted to 125 c.c. This was subjected to a current of $N.D._{100} = 0.03 - 0.05$ A and $V = 1.1 - 1.66$. The current acted from three to seven hours. The deposit of silver was free from copper.

The results varied from the theoretical by 0.0002—0.0003 grm. (see Table IV.).

Silver from Cadmium.—Smith and Spencer (*Journ. Am. Chem. Soc.*, xvi., 420) found that the deposition of silver was accelerated by heating the solution during the electrolysis, and that while cadmium may be entirely precipitated in the cold by the current, yet with a low current and a temperature of 60° the cadmium is held in solution. A separation of silver and mercury may thus be effected in a cyanide solution. In the same journal, Smith and Frankel record the separation of mercury from cadmium, zinc, nickel, and cobalt. In 1895 Smith and Wallace published later results with the same method. Following the data thus obtained, a solution of silver nitrate containing 0.1024 grm. of silver and cadmium sulphate solution equivalent to 0.168 grm. of cadmium was used. The salts were transformed into their double cyanides by an excess of potassium cyanide. The silver was obtained free from cadmium in four hours. The current used was $N.D._{100} = 0.02$ A and $V = 2.15$. The temperature was 60° before the current was passed through the solution (see Table V.).

The silver in all cases was found free from cadmium.

Silver from Zinc.—These metals were separated according to the following conditions:—Using zinc sulphate containing one-tenth grm. of zinc, and silver nitrate solution containing 0.1024 grm. of silver. The potassium cyanide used amounted to 1 grm. The solution was 125 c.c. in volume. It was electrolysed at 70° by a current of $N.D._{100} = 0.032 - 0.038$ A and $V = 2.76$. In three hours the deposition of the silver was complete (see Table VI.).

Nickel and cobalt were separated from silver in a similar way.

Silver from Nickel.—A solution of nickel nitrate containing one-tenth grm. of nickel was added to a silver nitrate solution, and both converted into the double cyanides by 1.5 grms. of potassium cyanide. The solution was electrolysed with a current $N.D._{100} = 0.02 - 0.03$ A and $V = 1.7 - 2$ for three hours. The separation in this time was found to be complete. The results show a variation from the calculated amount of ± 0.0001 grm. to -0.0002 grm. The solution of silver in nitric acid, when examined qualitatively, gave no evidence of the presence of nickel. The nickel solution, when examined, showed that the silver had been entirely precipitated (see Table VII.).

Silver from Cobalt.—Cobalt nitrate was the salt used in this separation. To the solution of silver nitrate (0.1024 grm. of silver) was added a solution of the cobalt salt containing 0.1 grm. of cobalt and 2.75 grms. of potassium cyanide. A current of $N.D._{100} = 0.02$ A and $V = 2.2 - 2.7$ at a temperature of 65° was passed through the solution for five hours. The silver in this time was entirely precipitated. No cobalt was found deposited with the silver (see Table VIII.).

Silver from Iron.—Heretofore these metals have not been separated electrolytically in cyanide solution. A solution of ferrous ammonium sulphate, equivalent to one-tenth grm. of metallic iron, was treated with sulphurous acid in order to reduce any ferric iron which might exist. After the reduction was complete, the excess of acid was nearly neutralised with potassium carbonate; to this, 2.5 grms. of potassium cyanide were added. The solution of the double cyanide, dark green in colour, was added to a solution of silver which had been converted into the double cyanide by five-tenths grm. of potassium cyanide. The entire solution was made up to 100 c.c. It was heated to 65°, and electrolysed with a current of $N.D._{100} = 0.04$ A and $V = 2.7$. At the expiration of three hours the

silver was found to be entirely deposited. There was in some cases a separation of ferric oxide at the anode. The silver, after its solution in nitric acid, was tested for iron by ammonium thiocyanate. A faint pink colour, due to a trace of iron in the acid used for the solution of the metal, was observed. The deposit, which was light grey in colour, varied but slightly from the theoretical amount of the silver present in the solution (see Table IX.).

(To be continued).

ON THE PROGRESS OF CHEMISTRY IN GREAT BRITAIN AND IRELAND DURING THE NINETEENTH CENTURY.*

PART I.—FROM THE BEGINNING OF THE CENTURY TO THE
FOUNDATION OF THE CHEMICAL SOCIETY (1841).

By T. E. THORPE, LL.D., F.R.S.,
President of the Chemical Society.

ALTHOUGH Century-summaries run a risk of being regarded as flat, stale, and unprofitable, I have ventured to think that it would not be uninteresting or altogether unuseful if, at this time, I sought to indicate in the broadest possible outline, what our countrymen have done during the past hundred years in gaining and extending knowledge within the special province of intellectual activity with which we, as a Society, primarily concern ourselves.

In examining the century's accounts, we naturally inquire into the nature of the balance with which it started. How much better it was felt to be than at the corresponding period of the eighteenth century may be gleaned from the circumstance that the Council of the Royal Society—actually the contemporaries of Newton—entered upon 1701 with the complaint, more petulant than dignified, that “the discouraging neglect of the great, the impetuous contradiction of the ignorant, and the reproaches of the unreasonable, had unhappily thwarted them in their design to perpetuate a succession of useful inventions.” During the years that followed, the achievements of Newton's successors, Franklin, Dollond, Maskeleyne, Canton, Priestley, Hunter, made the Fellows feel that they were not wholly dependent upon the patronage of the great, although as the battle over the lightning conductors too plainly showed, they were not altogether unmindful of the frowns and reproaches of the ignorant and unreasonable.

Let us then try to realise what was the state of things, so far as it may be thought to affect Chemistry and its pursuit, in the year 1800. To begin with, the population of these isles was less than half of what it now is. London contained only about 800,000 persons, and I need hardly say that the whole social and economic conditions of the people were vastly different from what they are to-day. In one respect, at least, the circumstances of this and that time were alike—we were at war. But the condition of the nation now is halcyon compared with what it was in 1800. England was then in such straits as she never was before. Her very existence as a nation was at stake. The harvest over a great part of the country had failed. Corn was upwards of £9 a quarter, and famine and pestilence brooded over the land. Whilst Napoleon's attempt at invasion had roused the nation to a defiant and stubborn resistance, the governing classes were torn asunder by party faction, and seemingly more eager to secure political supremacy than to devise means to resist the common enemy.

Under such untoward conditions, it might well be supposed that science would languish and decay. Such, however, was not the case. It is a singular fact, and the circumstance is not peculiar to our own history, that it is precisely during the lean years—during periods of national stress and strain—that some of our greatest intellectual

* Presidential Address to the Chemical Society, 1900.

triumphs have been won. In the history of Science, and especially of Chemistry, France was never more glorious than during the turmoil which preceded and followed the Reign of Terror; and in our own case never were such chemical triumphs achieved as during the gloomy period covering the dying years of the last century and the opening years of that which is now drawing to its close.

What then was the condition of chemical science in Great Britain in the year 1800? Who were its cultivators and what were they doing? Black had died in the preceding November; Priestley, who had suffered "the slings and arrows of outrageous fortune" in vainly buffeting with the times, had been settled some six years on the banks of the Susquehanna, occupying himself with his beloved theology and in futile efforts to resuscitate the dying doctrine of phlogiston. For, in 1800, phlogistonism had only been scotched in this country. Mr. Richard Kirwan, President of the Royal Irish Academy and Inspector-General of His Majesty's Mines in the Kingdom of Ireland, had, it is true, some years previously tried conclusions with the French chemists in his "Essay on Phlogiston," which had been translated by Mme. Lavoisier, in order to be refuted, point by point, by Lavoisier, Morveau, Laplace, Monge, Berthollet, and Fourcroy. The new theory was, in fact, indebted to this opposition for some of the strongest proofs on which it is founded. The nimble-witted Irishman found he was no match for this formidable battalion. He confessed himself vanquished, and, as he wrote to Berthollet, laid down his arms. Rather, he might have said, he went over to the enemy, for during the few years of activity which remained to him he preached the new doctrine with all the zeal of the convert, albeit a little restive at times under the tyranny of the nomenclature it imposed upon the chemical world. National prejudice, and the authority of Priestley and Cavendish, no doubt retarded its general adoption in this country. Cavendish, at the close of the last century, was in his 69th year; he had ceased to engage in chemical inquiry, although still keenly interested in its progress. James Watt, who played so notable a part in the events which led to the discovery of the composition of water, and younger by some five years than his quondam rival, was no longer actively occupied with chemical speculation. Wollaston, as dispassionate and hardly less reserved than Cavendish, was in his 34th year, struggling to get together the medical practice which his singularly cold and taciturn manner forbade him to expect. John Dalton, also in his 34th year, had just resigned his post as tutor at the Manchester Academy, where, as the Trustees were pleased to report, "he had uniformly acquitted himself to their entire satisfaction in the province of mathematics, natural philosophy, and chemistry," on the spacious salary of £80 a year, and was now looking out for pupils in those branches of learning at the rate of two shillings a lesson. Thomas Thomson was 27; Andrew Ure, of dictionary fame, was 22, the same age as Humphry Davy, who was still at the Bristol Pneumatic Institute, where he had published his "Researches, Chemical and Philosophical, chiefly concerning Nitrous Oxide." William Thomas Brande was a lad of 12; and little Michael Faraday, a child of 8, who lived in a mews near Manchester Square, keeping body and soul together on the weekly loaf he got from public charity, and while away his leisure in playing marbles in Spanish Place.

Of course the results of the more important chemical investigations of the period were laid before the Royal Society, and were published in the *Philosophical Transactions*, and subsequently in *Nicholson's Journal* or *Tilloch's Philosophical Magazine*. The Society at that time was, and had been for the previous twenty-two years, under the benevolent despotism of Sir Joseph Banks. The other officers were Wegg, Planta, Gray, and Layard. The meetings were held in the evening at 8 o'clock, and, of course, for the most part by candle-light, in one of the large rooms in Somerset House, or Somerset Place as it was then termed. The Society had moved,

in 1780, from Crane Court, into apartments provided for them by the munificence of their patron, George III., and the skill of his architect, Sir William Chambers, which habitation, in the language of the Council, "it was hoped would confer on them an external splendour in some measure proportional to the consideration in which they had been held for more than a century." Hard by was the Crown and Anchor Tavern, where the Royal Society Club held its pious orgies; the expense of the dinner was limited to five shillings, and black puddings were a standing dish. It is evident that the drowsy philosophers did no violence to their digestion by a too prolonged attention to the intellectual fare of the evening, for even a comparatively short communication not unfrequently occupied two if not three sittings. The President, when in town, lived in the then fashionable neighbourhood of Soho Square. Cavendish's town house was at the corner of Montague Place and Gower Street, and from here he might be described, in a faded violet court dress, frilled shirt front and wrists, with a great-coat of greyish-green, and a three-cornered cocked hat over his knocker-tailed periwig, slouching along, one hand behind his back, on the way to his library in Dean Street, Soho. Wollaston lived in Hunter Street, Brunswick Square, and subsequently in Dorset Street, Manchester Square; Smithson Tennant oscillated between his farm at Cheddar and his chambers in the Temple; and Charles Hatchett resided in the rural district of Hammersmith. Other notable chemical workers at this period were William Henry, of Manchester, William Haseldine Pepys, and Richard Chenevix.

There were, of course, other publishing agencies at work, with aims similar to those of the Royal Society, such as the Royal Society of Edinburgh, which grew out of a Society founded in 1731 by the leading medical men of that city; and the Royal Irish Academy, founded in 1782, and of which Kirwan was President for some years. Many of the provincial towns, too, had their Literary and Philosophical Societies, but with the exception of that at Manchester, to which the Henrys and Dalton were frequent contributors, their Proceedings and Transactions contain few important chemical memoirs during the first years of the century.

Theoretical chemistry was taught in the Universities, and in some of them, following the example set by Black, by means of experimental courses of lectures. At Oxford there had been Beddoes, but his political opinions were distasteful to the University, and he had resigned. At Cambridge there were F. J. Wollaston and Farish. Hope, who first made known the existence of strontia, lectured at Edinburgh; Robert Cleghorn at Glasgow; and Dr. French, who is credited with the saying that "Humphry Davy was a verri troublesome person in chemistry," taught at Aberdeen. Moreover, almost every large town had one or more teachers—men of the type of Varley, Garnett, and Aikin—who gave lessons at their private houses. Faraday relates how, during his bookbinding days, his master allowed him to go occasionally on an evening to hear the lectures delivered by Mr. Tatum, at his house in Dorset Street, of which he obtained knowledge by bills in the streets and shop-windows. The hour was 8 o'clock in the evening, and the charge was one shilling. More ambitious or more self-important people than Mr. Tatum announced their prospective courses among the *Miscellanea* of *Tilloch's* or *Nicholson's Magazines*. Thus, Dr. Beddoes informs the world that his "Lectures are to be calculated for both sexes and different ages; and that there may be little chance of exclusion by reason of narrow circumstances, the subscription is fixed at one guinea; but unless fifty persons shall have entered their names by the 31st of March, the Lectures will not go on, as without a tolerably numerous audience Dr. B. thinks he could bestow his time in a manner more advantageous to the public."

The principal manuals of the time were Kerr's translation of Lavoisier's "Elements"; Chaptal's "Elements,"

the standard text-book on applied chemistry; Parkinson's "Chemical Pocket-book or Memoranda Chemica"; Heron's "Elements"; Brisson's "Physical Principles of Chemistry"; Accum's "System of Theoretical and Practical Chemistry"; and Marcet's "Conversations."

The first two decades of this century are unquestionably the most momentous and the most brilliant of any period in the history of chemistry in our country. They witnessed the establishment of the fundamental laws of chemical combination and the atomic theory; the discovery of the so-called gaseous laws and of the real nature of the atmosphere; the application of voltaic electricity as an analytic agent; the isolation of the metals of the alkalis and of the alkaline earths; the determination of the chemical nature of the halogens; and in the discovery of tantalum, palladium, iridium, osmium, and rhodium, a considerable addition to the list of the metallic elements. These, in 1802, were only 23 in number, as against about 60 at the present time.

A number of new compounds were brought to light or identified during the same period,—such as fulminating mercury and fulminating silver, carbonic oxide, acetylene, phosgene gas,—for the most part substances deemed at the time of their discovery to be merely chemical curiosities, incapable from their very nature of being turned to useful account, but all of which are now of important practical application. The same period witnessed the invention of the reflecting goniometer and of the miner's safety lamp. It saw the establishment of gas-lighting, and with it the creation of an industry which has exercised a profound effect on the development of the chemical arts. It saw, too, the first attempt to control, by the aid of chemical analysis, the hygienic character of the drinking water supplied to a large community. The statement, in 1808, of Dr. Andrew Ure, who became Professor of Chemistry in Anderson's College in 1818, that the water from the wells in Glasgow, which were then the chief sources of supply, contained "a surprising quantity of heterogeneous matters in solution," paved the way for the action of Telford and Robertson Buchanan in bringing in "the inexhaustible supply from the River Clyde by means of pipes and steam-engines." In the *Philosophical Magazine* for 1808 we read that this was the first occasion on which the whole of a public supply was filtered "by means of reservoirs constructed for the purpose. . . . This salutary process is effected by making the water filter through sand and gravel from the large reservoir into which it is first elevated by the steam-engine into a second reservoir posited a little lower, and from which the conveying-pipes receive their supply." It is not often that Glasgow is willing to take a lesson from Paisley, but it is interesting to read that a Paisley "buddy" first practised the filtration of water intended for public supply, and it is satisfactory to learn further that "this public spirited adventurer was amply remunerated for his expenditure."

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th instant, The Duke of Northumberland, K.G., President, in the Chair. The following were elected members:—Mrs. E. S. Beale, E. Callard, E. J. Duveen, E. Pearson, Lord Russell of Killowen, and J. A. Thierry. The special thanks of the Members were returned to Professor F. Clowes for his donation of £20 to the fund for the Promotion of Experimental Research at Low Temperatures. The Chairman announced that he had nominated the following Vice-Presidents for the ensuing year:—Sir F. Bramwell, Right Hon. Lord Lister, Dr. Ludwig Mond, Sir Andrew Noble, Mr. A. Siemens, the Hon. Sir J. Stirling, Sir J. Crichton Browne, and Sir William Crookes.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

A CONVERSAZIONE was held at the Society's Rooms, Burlington House, on Wednesday evening last, May 9th, the Fellows and guests being received by the President, Lord Lister, and the members of the Council.

Among the numerous interesting exhibits may be mentioned Messrs. H. B. Hartley and H. L. Bowman's demonstration of the properties of crystals yielding doubly-refracting liquids on fusion.

Certain crystalline organic compounds, viz., *p*-azoxy-anisole, *p*-azoxyphenetol, and cholesteryl benzoate, have been found by Prof. Lehmann, of Karlsruhe, to give on melting (at temperatures of 116°, 134°, and 145° respectively) liquids possessing the properties of double-refraction and dichroism, even under conditions in which a state of strain is impossible. When these anisotropic liquids are further heated, they change at definite temperatures of transition (134°, 165°, and 178° respectively) into ordinary isotropic liquids. The intermediate bodies have been called "liquid crystals," for, although the evidence of their elasticity, viscosity, and dielectric capacity shows them to be undoubtedly liquids, yet nevertheless they possess, like crystals, both double-refraction and dichroism.

Another exhibit, which shows the possibility of directing the movements of torpedo boats, &c., at a distance, is shown by Mr. Richard Kerr, who has a clock to which a coherer is attached: a transmitter, in another part of the room, gives rise to ethereal waves on the Hertzian system; these acting on the coherer set the clock in motion.

Dr. Downing has some interesting maps showing the path of the total eclipse of the sun on May 28th next: this eclipse will be partially visible in London, viz., three-fourths of totality.

Mr. Thomas Thorp shows some celloidin grating films and their application to diffraction colour photography. Celloidin films of diffraction gratings, of about 14,500 lines to the inch, are impressed on chromated gelatin plates, the surface of which thus becomes grooved. Light falls on the gelatin surface through photographic transparency. The celloidin film is detached, and the plate immersed in warm water, when the image appears in grooves more or less decided. Pictures are superposed and illuminated, and are then seen in their natural or other desired colours stereoscopically.

Flashes induced by Hertz waves in a helium tube were shown by Prof. Minchin, and a number of examples of leadless glazed ware by Dr. T. E. Thorpe.

Some very good specimens of apparatus constructed of vitreous silica were shown by Messrs. W. A. Shenstone and H. G. Lacell. These specimens are a distinct advance on those exhibited last year.

A very delicate electric micrometer is exhibited by Mr. P. E. Shaw, by means of which movements as small as 1/200th of a wave-length of sodium light have been measured.

A variety of explosives, a few experiments, and the results of others, with models showing the effect of erosion in guns, were shown in the Meeting-room by Sir Andrew Noble at 9.45 o'clock.

At 10.30, Dr. A. W. Rowe gave a short demonstration of the photo-micrography of chalk fossils by reflected light; and at 11.15 Mr. F. Enoch showed on the screen a series of photographs showing the metamorphoses of one individual nymph of *Æschna cyanea*, from the moment of quitting the water to that of the perfect imago.

NOTICES OF BOOKS.

Practical Chemistry. Part I. By WILLIAM FRENCH, M.A. (Cantab.), F.I.C., F.C.S. London: Methuen and Co. 1900. Pp. 136.

AFTER having gone through a preliminary course of laboratory work, such as weighing, thermometry, the use of burettes, and other apparatus, cork-boring, &c., the student should be able to go through the course of experimental chemistry as herein described without any difficulty or necessity for very minute instructions. The author's statement that his "object has been throughout the book to give the students as little information about the experiments as possible," is badly expressed; he gives ample explanations and directions for carrying out the experiments successfully, but does not overburden his instructions with unnecessary details. It should be remembered that most students take up the subject of chemistry voluntarily, and should be able to make observations and deductions from simple experiments, such as we here find, without much help.

The contents of this book are decidedly elementary, and go little beyond the simplest practical work. The subjects dealt with are mainly evaporation and distillation, filtration, and crystallisation, the constituents of air and water, earthy bodies such as chalk and lime, experiments with common soda, salt, and such like.

The appendices comprise a few details of fitting up apparatus, and a number of questions and exercises.

Aids to Practical Pharmacy for Medical Students. By A. CAMPBELL STARK. Revised according to Pharmacopœia of 1898. London: Baillière, Tindall, and Cox. 1900. Pp. 170.

SMALL as this book is, it contains all the information necessary for a student who offers himself for examination in practical pharmacy of the Conjoint Board. After a few general remarks on pharmaceutical processes, medicinal preparations, prescribing, &c., a list of the substances used in pharmacy is given; this is divided into Part I., Inorganic Substances, and Part II., Organic and Vegetable Substances, in which their production, principal characteristics, preparation, and doses are described. In Part II. the drugs are arranged in groups, those drugs with similar pharmacological properties being placed together.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 15, April 9, 1900.

Density and Analysis of Sulphur Perfluoride.—H. Moissan and P. Lebeau.—By the action of excess of fluorine on sulphur the authors obtained a new gaseous body (sulphur perfluoride) having a formula SF_6 . This gas is one of the heaviest known, its density being 5.03. The composition of this substance proves the hexatomicity of sulphur in a simple manner; it corresponds to sulphuric anhydride, SO_3 . Its examination is very interesting, owing to the inertness of its properties. Two such active bodies as sulphur and fluorine, when united to saturation, give a compound which is not attacked by melted potash or by sodium at its fusion point. This new sulphur fluoride is totally different from the known chlorides of sulphur.

Heat of Formation of Hydrated and Anhydrous Strontium Dioxide.—M. de Forcrand.—A comparison of numbers obtained by the author shows that the heat of peroxidation of anhydrous SrO is inferior by 1 cal. to that of BaO . This explains the fact that anhydrous strontium dioxide is less stable and less easy to obtain than the protoxide. Its dissociation tension is greater. These numbers also show that this is the inverse of the precipitated hydrated state. Strontium dioxide has a greater affinity for water by 2 cal. than barium dioxide. As a result of this, hydrogen peroxide acts on dissolved strontia, evolving nearly as much heat as a strong acid, and giving a precipitate, $\text{SrO}_2 \cdot 9\text{H}_2\text{O}$, which is the hydrated neutral salt.

A New Method of Fractionation of some Rare Earths.—Eug. Demarcay.—The author, in 1896, announced that samarium, of atomic weight 150, contained another element characterised by spectrum lines in the violet and ultra-violet. Since then he has been occupied in the isolation of this element. All known methods of fractionation apparently failed to isolate it, but a separation can be effected by the crystallisation from nitric acid of the double nitrate of magnesium and the rare earths. This double salt corresponds to the general formula $\text{M}_2(\text{NO}_3)_6 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$. The lanthanum salt is the least soluble in nitric acid. Large quantities of pure samarium can be obtained by this method, whilst the new element is always associated with gadolinium, and so separated from samarium.

Formation of Monomercurammonium Iodide by the Action of Concentrated Ammonia on Mercurdiammonium Iodide.—Maurice François.—Concentrated ammonia, when added in large excess to mercurdiammonium iodide, allows of the formation of monomercurammonium iodide, HgH_2NI , a body which has not previously been described. This iodide must be dried in a strongly ammoniacal atmosphere, and then extracted with pure ether, to eliminate the mercurdiammonium iodide. It is a white substance formed of microscopic crystals, differing from mercurdiammonium iodide in that it does not redden in the air and is not soluble in ether.

Crystalline Selenide of Manganese and an Oxy-selenide.—M. Fonze-Diacon.—(1) The author obtained the cubic manganese selenide, MnSe , (a) by the action of SeH_2 on a solution of manganese acetate slightly acidulated with HCl , (b) by the reduction of selenate of manganese in the electric furnace by means of carbon, and (c) by the fusion of precipitated manganese selenide at a high temperature. (2) He obtained a prismatic manganese selenide, MnSe , by the action of SeH_2 on manganese chloride at a red heat. (3) By reducing manganese selenate by means of hydrogen at a high temperature, green oxy-selenide of manganese was prepared.

Reducing Action of Calcium Carbide.—M. Geelmuyden.—Moissan has previously noticed the reducing properties of calcium carbide, and the reactions which take place in the presence of oxides. The author examines the action of calcium carbide on various other substances in the electric furnace. The commercial material was used for these experiments, and its action on boric anhydride and several metallic sulphides examined.

New Method of Production of Double Sulphates of Chromium.—C. Pagel.—When sulphuric acid acts on bichromate of potash and potassium chloride, only hexagonal crystals are obtained. When, however, bichromate of soda and pure sodium chloride are used, a prismatic salt is obtained. These crystals are insoluble in water and acids, and are not attacked by soda solution in a sealed tube. When heated on platinum foil they become reddish violet, and on cooling re-take their green colour. Analysis shows them to have the composition Cr_2O_3 , 18.5; SO_3 , 58.62; $\text{SO}_4 \cdot \text{Na}_2$, 52.24. Numbers which correspond to the formula $(\text{SO}_4)_3\text{Cr}_2 \cdot 3\text{SO}_4 \cdot \text{Na}_2$.

Electrolytic Estimation of Lead in Sulphates and Chromates. Application to the Analysis of Lead Glass and Lead Chromates.—C. Marie.—The lead sulphate is placed in a glass electrolytic cell, then attacked by nitric acid, crystals of ammonium nitrate being added little by little. When the sulphate has completely disappeared, the whole is diluted with hot water, and electrolysed under ordinary conditions, keeping the temperature at 60–70°. The lead dioxide is weighed on the electrode. This method can be applied to the analysis of lead glass, by adding HF to the finely-powdered glass, and a sufficient quantity of sulphuric acid to transform the bases into sulphates. Chromate of lead dissolves in nitric acid, and ammonium nitrate still more easily than the sulphate.

α - β -Trimethyl- β -oxyadipic Acid.—E. E. Blaise.—The methyle ether of the lactonic acid corresponding to the $\alpha\beta$ -trimethyl- β -oxyadipic acid, has been obtained by condensing methyl levulate and methyl bromoisobutyrate in presence of zinc. The bromozincic derivative thus formed is then decomposed by dilute sulphuric acid. This condensation only gives a yield of about 15 to 17 per cent.

Action of Amyl Chloride on Calcium Carbide.—P. Lefebvre.—By passing the vapour of amyl chloride over calcium carbide heated to redness various products are obtained. The liquid products, when fractionally distilled, separate into products not containing chlorine boiling below 45°, and products containing chlorine boiling above 75°. These products were analysed and identified as far as possible. The analysis of the gases obtained showed the presence of acetylene, ethylene, other ethylenic carbides, hydrogen, and nitrogen.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 1.

Normal Presence and the Localisation of Arsenic in the Organs of Animals.—A. Gautier.—Already inserted (p. 135).

Malates and Tartromalates.—Ch. Ordonneau.—Tartromalate of lime α is prepared in the pure state by treating crude tartrate of lime with boiling water. The filtered liquid, after cooling for twelve hours, gives 5 or 6 grms. per litre. Under the microscope it appears in long silky needles. When air-dried, it contains 9 to 10 H₂O. 100 c.c. of distilled water at 20° dissolved 0.27 gm. of this salt, but it is much more soluble in boiling water, by which it is, however, partially decomposed. The same salt is obtained by mixing equal weights of tartaric and malic acids, saturating with ammonia, and precipitating the solution with excess of acetate of lime, added all at once. The author also describes the preparation and properties of malate of lime α , tartromalic acid α , bimalate of lime, malate of lime β , tartromalate of lime β , and tartromalic acid β .

Some Chloranisidines and *m*-Chloranisol.—F. Reverdin and F. Eckhard.—To decide the question as to whether or no there was a migration of the halogen in the nitration of *p*-chloranisol, the authors took up the comparative examination of the nitration of the ortho- and para-chloranisols, and they made use of the opportunity to examine the characteristics of the derived chloranisidines. The three substances are easily recognised by means of their nitrated derivatives; the *o*-chloranisol, on nitration, gives *o*-chlor-*p*-nitranisol, fusible at 95°, not distilling with steam; *p*-chloranisol gives *p*-chlor-*o*-nitranisol, fusible at 98°, distilling with steam; finally, under the same conditions, *m*-chloranisol gives a derivative fusible at 58°, distilling with steam.

On Dissymmetric Tetramethyldiamidodiphenylethane.—A. Trillat.—This body occurs as a white mass, perfectly crystallised, in the form of flakes fusing at 68–69°; it is insoluble in water, but soluble in alcohol, ether, ligroin, chloroform, and all dilute acids, with which it

forms well crystallised salts. When exposed to the air it takes a red tinge, probably due to some intra-molecular transposition.

Examination of some Derivatives of Leucobase, C₁₈H₂₄N₂.—A. Trillat.—If leucobase is dissolved in acetic acid, and a little binoxide of lead be added, a beautiful greenish-blue colour immediately appears, and carbinol is formed. This organo-plumbic compound is decomposed by soda after two hours, the hydrate of lead being dissolved and the base left. This treatment is repeated several times, and the base then washed with boiling water; when dry, it appears as a brown mass, soluble in all acids, but particularly so in acetic acid, taking a blue colour. The author then describes a number of salts, such as the chloroplatinate, the acid sulphate, the acetate, phosphate, oxalate, bromethylate, &c., and the nitrated, bromised, and iodised derivatives.

Action of Nitrous Acid on Leucobase, C₁₈H₂₄N₂.—A. Trillat.—Already noticed.

Action of Chloride of Aluminium on Camphoric Anhydride.—G. Blanc.—Already noticed.

Benzoylfurfurane.—R. Marquis.—Already noticed.

Action of Hydroxylamine and Phenylhydrazine on Dithiobenzoylacetone.—V. Vaillant.—Dithiobenzoyl-

$$\text{C}_6\text{H}_5-\text{CO}-\text{CH}=\text{CO}-\text{CH}_3$$
 acetone,
$$\text{C}_6\text{H}_5-\text{CO}-\text{CH}=\text{CO}-\text{CH}_3$$
 of which a certain number of reactions have already been described, combines easily with hydroxylamine and phenylhydrazine, giving the corresponding oxazol and pyrazol.

The Essences of Geranium.—MM. Jeancard and Satie.—The authors have examined essences of geranium from six different sources. The solubility of all of them in alcohol is practically the same; that is, 1 volume of essence dissolves in 0.9 to 1 vol. of alcohol at 80°, or in 2 to 2.3 vols. at 70 per cent at 15°. They contain variable quantities of acids, and become oxidised on contact with the air. That from Cannes contains the least free acid and oxidises the least rapidly.

Absorption of Iodine by Plants.—P. Bourcet.—Already inserted in full (p. 110).

On a Cause of Error in Testing for Sugar in Urine by means of Fehling's Solution.—J. Eury.—The presence of sugar in urine must not be assumed only when a precipitate of suboxide of copper is formed by the cupropotassic solution. When a urine containing a large amount of sugar is heated with cupro-potassic solution, a rapid decolouration is observed, while the liquid remains limpid. When left to itself, the upper part becomes rapidly of a reddish brown colour, and a brown precipitate is soon formed throughout the tube. This is due to an oxidation only produced by heat, but the precipitate is not suboxide of copper, and it must not therefore be concluded that sugar is present. The reaction is found to be due to the presence of creatinic bases.

Estimation of Phosphorus in Organic Compounds.—Ch. Marie.—Already noticed.

The Salts of Pyropervanadic Acid.—P. Melikoff and L. Pissarjevsky.—By treating the metavanadates with H₂O₂ we obtain the salts VO₄M. If we add an excess of alkali to the H₂O₂ we obtain the yellow compounds, V₂O₁₁(NH₄)₄ and V₅O₂₆K₈·2H₂O, which are considered by the authors to belong to pyropervanadic acid, the potassic salt being 3VO₄K₂O₂ + 2VO₄K + 2H₂O. By dissolving this latter salt in H₂O₂, adding KOH, cooling the mixture to 0°, gradually adding H₂O₂ until the green colour no longer changes, and precipitating with alcohol, we obtain a fluorescent precipitate having the formula V₂O₉K₂·3½H₂O, that is to say, a compound of pyropervanadic acid with K₂O₂. All these compounds are fairly stable in the dry state.—*Journ. Soc. Phys. Chim. R.*, xxvi., p. 108.

MISCELLANEOUS.

Volumetric Estimation of Bismuth by Means of Arsenious Acid in Alkaline Solution.—C. Reichard.—This method consists in transforming the bismuthic compound into Bi_2O_3 by means of a current of chlorine in alkaline solution. Wash by decantation to remove the Cl and NaOH. Add excess of a solution of As_2O_3 in potash or soda-lye, and boil until the red precipitate becomes white. Filter and estimate the remaining As_2O_3 with permanganate.—*Zeit. Anal. Ch.*, xxxviii., p. 100.

Digestion of Fibrine and Albumen by Papaine, and on a New Coloured Reaction of the Products obtained.—V. Harlay.—Three digestions were made with a papaine which dissolved fibrine rapidly: *a* was in a solution containing 0.2 per cent. of HCl; *b* contained 0.2 per cent. of bicarbonate of soda; and *c* was in simple aqueous solution. All three contained 0.10 gm. of papaine per 50 c.c., and were made to act on 5 grms. of fibrine. They were heated to 40–45° on the water-bath. The disaggregation was almost as rapid in *b* as in *c*, and almost total in two hours and a half. In *a*, there was first swelling and then solution, but even after six hours there still remained a considerable amount of fibrine, swollen but not dissolved. The liquid *a* was difficult to filter, but *b* and *c* filtered easily; the polarimeter showed that the action in *b* was less advanced than in *c*. All three liquids gave with tyrosinase the characteristic colouration—first red, then green,—but the two former had to be first neutralised. The colouring-matters produced by the action of tyrosinase on papain and pepsic liquids and digestions are identical; and, in the case of pepsic digestion, this colouring-matter is accompanied by other colouring-matters, which are the first destroyed by reduction with zinc and hydrochloric acid. This reaction distinguishes papain from pancreatic digestion, and separates it from pepsic digestion.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xi., No. 4.

Some Compounds of Iodantipyrine with the Mercuric Salts.—J. Bougault.—When 3.14 grms. of iodantipyrine, dissolved in 30 c.c. of warm alcohol at 95°, is mixed with a solution of 2.71 grms. of bichloride of mercury in 20 cubic centimetres of alcohol at 95°, there are deposited, on cooling, beautiful colourless crystals of $\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O} \cdot \text{HgCl}_2$. This compound melts at 168–169° with decomposition. It is almost insoluble in hot or cold water; it is slightly soluble in cold alcohol, and insoluble in ether. The bi-iodide of mercury does not combine directly with iodantipyrine under similar circumstances, though bi-iodide of mercury combines easily with antipyrine, forming $(\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O})_2 \cdot \text{HgI}_2$. The compound $(\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O})_4 \cdot \text{HgCl}_2 \cdot \text{HgI}_2 \cdot 2\text{HCl}$ is formed by the action of iodine on antipyrine in the presence of an excess of sublimate in alcoholic solution; when the solutions are sufficiently concentrated, the crystals are deposited; they are white or pale yellow in appearance, and melt with decomposition at about 140°. This body is also decomposed very rapidly by water; the rose tint of the bi-iodide of mercury rapidly appears, and the hydrochloric acid goes into solution with a little of the mercuric salt. The compound $(\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O})_2 \cdot \text{HgI}_2 \cdot \text{HCl}$ is obtained by the action of iodine on antipyrine in alcoholic solution in the presence of a definite quantity of sublimate (2 mols. of HgCl_2 for 4 mols. of $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}$). This body occurs in crystals having a beautiful yellow appearance; it melts with decomposition at 130°; with regard to the action of solvents, it behaves exactly the same as the body $(\text{C}_{11}\text{H}_{11}\text{IN}_2\text{O})_4 \cdot \text{HgI}_2 \cdot \text{HgCl}_2 \cdot \text{HCl}$.—*Journ. de Pharm. et de Chimie*, Series 6, vol. xi., No. 4.

Tungsten.—A. Stavenhagen.—To prepare metallic tungsten the author took an intimate mixture of pure tungstic anhydride and aluminium filings, also as pure as possible (2 mols. Al to 1 mol. WO_3); 300 grms. of this

mixture were placed in a clay crucible, and the fire started by means of a magnesium ribbon, ending in a cap formed of BaO_2 , and Al filings. The reaction is almost explosive, and a part of the contents of the crucible are thrown out. After cooling, we find disseminated through the slag, a friable, porous, metallic mass consisting of tungsten containing 2.6 per cent. of aluminium, not attacked by acids, even aqua regia, easily attacked by melted KOH. To obtain melted tungsten, the author, after having proceeded by deflagration as just described, added a certain quantity of sheet aluminium to the mass, and submitted the whole to the action of a large oxygen-hydrogen flame; after fusion he continued to inject oxygen alone; the excess of aluminium was thus burnt off, and after cooling, a button of tungsten was found under the slag, not containing more than 0.5 per cent. of aluminium, in a crystalline mass, in colour a little darker than zinc, and scratching glass; its density was 16.6; it is unattacked by acids, and slowly attacked by melted KOH. Tungsten only melts superficially in the Moissan furnace; it loses its aluminium, but has a tendency to become carburised. As it is a bad conductor of electricity, it does not directly receive the effect of the voltaic arc, which prefers going round by a path of less resistance.—*Berichte*, xxxii., p. 1513.

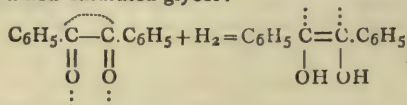
The Chemistry of Mercury.—H. Ley and H. Kissel.—The authors have examined the electric conductivity of the solutions of a certain number of mercuric salts, with a view to determining their constitution; they start with the principle that the hydrolysis of these salts in the cold is much more marked (in the same way as the electric conductivity of water is increased), if the mercury is united directly with the oxygen, than if it is in direct relation with another metalloid (N, C, Cl). This latter is the case with the chloride, bromide, and cyanide of mercury as well as the acetamide, succinamide, and even mercuric glycol, which seems to show that in this latter case the

glycol has taken the form $\begin{array}{c} \text{NvH}_3 \cdot \text{CH}_2 \\ | \quad | \\ \text{O} \text{---} \text{CO} \end{array}$. The first case

(strong hydrolytic dissociation), on the other hand, is met with in the salts of oxygenated acids, such as mercuric acetate, chloracetate, propionate, glycolate, and perchlorate. The authors then pass to the examination of some nitrated salts. Mercuric nitrite may be compared with the acetate, the mercury is attached to the oxygen. The mercuric salt of methylnitramine (fine, hard needles, slightly soluble in water), is also easily dissociated in its solutions; methylnitramine must therefore be regarded as a hydroxylised body, $\text{CH}_3 \cdot \text{N} = \text{NO} \cdot \text{OH}$. On the other hand, fulminate of mercury behaves like the cyanide, from the point of view of its decomposition by water and its electric conductivity; we know that these two salts react in a similar manner with regard to sodium amalgam, being transformed into a sodic salt. It is therefore probable that fulminic acid, $\text{C} = \text{N} - \text{OH}$, undergoes, in its mercuric salt, a tautomeric transformation which places H in connection with C, or with N, as happens with various oximes. Mercuric nitroform, $[\text{C}(\text{NO}_2)_3]_2 \text{Hg}$, is obtained easily by agitating an ethereal solution of nitroform with HgO ; it occurs in colourless prisms, extremely soluble in ether, giving a colourless solution; it behaves in the same way with benzene, chloroform, and acetic ether. Its solutions in alcohol, acetone, and acetaldoxime is of a pale-yellow colour; its solutions in water, pyridine, and benzonitrile are strongly yellow. With water this colour comes from dissociation; with pyridine from combination. The aqueous solutions are acid, and are dissociated very easily; the authors, agreeing with the views held by M. Hantsch (*Ber.*, xxxii., 580), think that the salt, either solid or dissolved in non-dissociating solvents, is a metallic derivative or pseudo-salt, with Hg near to C, while in an aqueous solution, there is a formation of free nitroform and of a derived basic salt, of a hydroxylised tautomeric form.—*Berichte*, xxxii., p. 1357.

The Salts of Perboric and Pertitanic Acids.—P. Melikoff and L. Pissarjevsky.—The authors have arrived at the following conclusions:—Perboric acid, BO_3H , with the alkaline metals forms soluble salts fairly stable in the dry state. The salts of the alkaline-earthly and the heavy metals are either only slightly soluble or else insoluble. The acid BO_3H with the peroxides only gives extremely unstable compounds. Besides the acid TiO_3 , there is still probably an acid Ti_2O_7 . Both of them easily form either basic or neutral compounds with the peroxides of the alkaline and alkaline-earthly metals. All these compounds are fairly stable.—*Journ. Soc. Phys. Chim. R.*, xxx., p. 693.

The Reduction of Benzile.—J. Thiele.—According to a previous paper, the reduction of benzile ought to give rise to a non-saturated glycol:—



But this latter is unstable, and is immediately transformed into benzoin. If the reduction is effected in the presence of acetic anhydride, the glycol can be isolated in the form of diacetic ether. This glycol is not a product of transformation of benzoin, as this latter gives an acetylated derivative directly when treated with acetic anhydride. The diacetic ether of diphenylglycol occurs in two stereoisomeric forms (ethylenic isomers). The reaction is produced in the following manner:—50 parts of benzile are dissolved in 300 parts of acetic anhydride; then, after cooling, a mixture of 50 c.c. of sulphuric acid and 100 c.c. of acetic acid are added. To the liquor, kept at 30 to 40°, 60 grms. of powdered zinc are gradually added. The solution is then precipitated with water, exhausted with ether, and crystallised in benzene. The less soluble modification α is first deposited in the form of white needles, fusible at 153°, slightly soluble in organic liquids; the more soluble isomer β crystallises in flakes, fusible at 110°. Alcoholic potash saponifies both the diacetates, giving benzoin. Permanganate oxidises them easily, but bromine does not have much effect. By heating the isomer β for five hours with acetic anhydride it is transformed, to a very small extent, into the isomer α .—*Ann. Chem.*, cccvi., p. 142.

MEETINGS FOR THE WEEK.

- MONDAY, 14th.**—Society of Arts, 8. (Cantor Lectures). "The Incandescent Gas Mantle and its Use," by Prof. Vivian B. Lewes.
- TUESDAY, 15th.**—Royal Institution, 3. "Brain-Tissue considered as the Apparatus of Thought," by Alex. Hill, M.A., M.D.
- WEDNESDAY, 16th.**—Society of Arts, 8. "A National Repository for Science and Art," by Prof. Flinders Petrie.
- Microscopical, 8. "On the Lag in Microscopic Vision," by E. M. Nelson, F.R.M.S. Preceded at 7.30 by an Exhibition of Microscopic Pond Life.
- Institution of Mining and Metallurgy, 8. "Presidential Address," by C. Algernon Moreing (President). "The Mineral Resources of New Caledonia," by F. Danvers Power, M.I.M.M. "Notes on Gold and Silver Amalgamation," by W. S. Welton, M.I.M.M.
- THURSDAY, 17th.**—Royal Institution, 3. "A Century of Chemistry in the Royal Institution," by Prof. Dewar, M.A., LL.D., F.R.S.
- Chemical, 8. "Chlorine Derivatives of Pyridine—VI. The Orientation of some Aminochloropyridines," by W. J. Sell, M.A., and F. W. Dootson, M.A.
- Society of Arts, 4.30. "The Industrial Development of India," by Jervoise Athelstane Baines, C.S.I.
- FRIDAY, 18th.**—Royal Institution, 9. "The Structure of Metals," by Prof. J. A. Ewing, M.A., F.R.S.
- SATURDAY, 19th.**—Royal Institution, 3. "South Africa—Past and Future," by Dr. Alfred Hillier.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2112.

THE ACTION OF CHLORIDE OF CALCIUM ON SILICATES.

By A. TIXIER.

WHEN a silicate is heated to redness with chloride of calcium, chlorine is given off if the calcination is effected in a current of air, and hydrochloric acid if we direct a current of steam on to the red-hot mixture. This reaction has even been the subject of many applications for Solvay patents since 1877, either with regard to the principle itself or for the methods of application. The Solvay patents particularly mention the use of silica, alumina, silicates of alumina, clays, &c., which, it is true, are the most common. They make no allusion to the more complex silicates, such as the feldspars, lepidolites, petalites, &c. Further, there does not appear to have been published any work mentioning the nature of the reactions which occur during this method of treating chloride of calcium with the object of utilising the chlorine, nor on the influence of the composition of the mixture on the result. The present paper fills up these gaps, and will further show that secondary reactions take place which are capable of important commercial applications.

When we heat a silicate with chloride of calcium, if the silicate contains alkalis they are transformed into chlorides, which are easily removed by simply washing with water. If the calcination is effected in a current of air, chlorine is given off, mixed with a certain quantity of hydrochloric acid, coming either from the water of hydration of the silica or from the moisture remaining in the mixture.

The return of chlorine depends essentially on the composition of the silicate and its proportion with regard to the CaCl_2 ; the amount of chlorine liberated is so much the greater, under identical circumstances, as the silicate is richer in silica and poorer in alkalis and in aluminium. The maximum returns in chlorine were obtained with pure silica. By this means, as much as 96 per cent of the total chlorine was recovered, of which 90 per cent was in the form of free Cl_2 and 10 per cent in the state of HCl . When the object of the reaction is only to produce chlorine, it is thus not advantageous to use silicates of alumina. The proportion of silicate with regard to the chloride has also a great influence on the return. This increases with the proportion of silicate, but only up to a certain limit; after that an excess is a disadvantage; this limit is further reduced when, at the same time as the production of chlorine, we want to collect the alkali from the silicate. In both cases excess of silicate makes the mass, which has till then kept porous, more fusible, and thus diminishes the action of the air; it also reacts on the alkaline chlorides formed, giving insoluble complex chlorosilicates, from whence arise losses in chlorine and in alkali.

The experiments described in this paper were carried out with the following materials:—Pure alumina, lepidolite, kaolin, petalite, artificial silicate of alumina, and silicates from various sources. The experiments were made with the double object of obtaining maximum quantities of chlorine, and, in the case of silicates containing alkalis, especially lithia, of extracting these alkalis under the most favourable conditions.

The following was the composition of the materials used:—

Alumina.—The pure commercial product used in the manufacture of aluminium.

Lepidolite—

Loss at a red heat	..	4'15	
Silica		54'50	or 56'08 per cent of the anhydrous mineral.

Alumina		29'80	
Oxides of Fe and Mn..		Traces	
Lime		Traces	
Potash		9'00	
Soda		Traces	
Lithia		2'80	
Fluorine		Traces	

Kaolin—

Loss at a red heat	..	13'00	
Silica		52'00	or 59'77 per cent of the anhydrous substance.

Alumina		36'05	or 40'23 per cent of the anhydrous substance.
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Petalite—

Loss at a red heat	..	1'4	
Silica		74'50	
Alumina		20'75	
Oxide of iron		Traces	
Lime		3'00	
Lithia		2'30	

Artificial Silicate of Alumina—

Moisture		51'00	
Silica		39'00	or 79'05 per cent of the anhydrous substance.

Alumina		4'50	
Soda		5'50	

Silicas containing from 85 to 99 per cent of SiO_2 (differences=water, lime, alumina).

Experiments with regard to the Manufacture of Chlorine.

—The apparatus consists of a porcelain tube heated over a row of burners and enclosed in an iron tube. A current of dry air is forced in at one end, the other end of the tube is connected with two flasks, followed by a vertical tube filled with glass beads. By a very simple arrangement the smell can be judged towards the end of the operation without disconnecting the apparatus, and with hardly any loss. The method of working is as follows:—A double normal solution of pure chloride of calcium is used, taking 50 c.c. for each operation; that is equal to 3'55 grms. of chlorine. This solution is evaporated to dryness with the corresponding silicate in a small porcelain crucible, while constantly stirring with a glass rod. The dry material is then detached and placed in the tube—either in a porcelain boat, or, if the volume is too great, in the tube itself. The crucible and the glass rod are both rinsed with distilled water, and the chlorine in solution estimated; thus, by difference, we get the quantity of chlorine placed in the tube. Heat to redness, and then pass dry air through at the rate of three bubbles a second. The first washing flask contains 50 c.c. of a double normal solution of arsenite of soda (1 litre=71 Cl), which absorbs the Cl and HCl . The second flask and the vertical tube contain water tinted with litmus. After the operation, which lasts four hours, the Cl set free and the total Cl are estimated. The contents of the first wash-bottle are diluted to 500 c.c., and the remaining As_2O_3 , and thus the Cl_2 absorbed, is titrated with $\text{N}/5$ iodine in this solution. The total chlorine is estimated by precipitation by means of NO_3Ag in nitric solution. The contents of the tube are further washed with distilled water; in this solution (filtered) the Cl is estimated; the insoluble residue is attacked with nitric acid, and the Cl again estimated in this fresh solution. In this manner the whole of the chlorine is accounted for, and the amount lost during the operation is estimated. The following is an example of the method of working (Experiment 20 in

the table):—Action of silica on chloride of calcium in the proportion of $2\text{CaCl}_2 : \text{SiO}_2$.

Dry together { 50 c.c. of $2\text{N}\text{CaCl}_2$ solution = 3.55 Cl.
9.5 grms. anhydrous silica.

The product is detached, and there remains adhering to the crucible 0.054 Cl. Calcine for four hours in a current of air (3 bubbles a second); the residue, after calcination, weighs 5.96 grms.

The chlorine recovered is—

	Grms.	
In the drying crucible . . .	0.054	
Given off as free Cl_2 . . .	1.003	Total, 1.263
Given off as free HCl . . .	0.260	
		grm.

Chlorine in the residue from calcination—

Soluble in water . . .	1.769
Soluble in NO_3H . . .	0.386

Total . . .	3.472
Loss (3.55 - 3.472) . . .	0.078

There is therefore given off—

$$\frac{1.263}{3.55 - 0.054} = 36.1 \text{ per cent of total Cl, containing—}$$

$$\frac{1.003}{1.263} = 79.4 \text{ per cent of free chlorine.}$$

The experiments made with regard to the production of chlorine are given in the accompanying table. At the same time the return of lithia is given; this shows the influence of the excess of silicate. The figures given in this table are, above all, of relative value; for, of all the operations, which were made under identical conditions of heating and duration (four hours at a cherry-red heat), none was pushed to the extreme limit of exhaustion; the most important action, the liberation of chlorine, became slower and slower, though it never ceased entirely.

Experiment 26 was made under conditions which enabled an account to be kept of the variations in the liberation of the chlorine. The gases, on leaving the porcelain tube, passed through a drawn-out tube into a beaker containing a solution of iodide of potassium and starch. The chlorine as it passed over displaced the iodine, which coloured the solution blue. By the aid of a graduated burette, a titrated solution of arsenite of soda was added, so as to keep the solution colourless. In this way it was found that—

During the first hour . . .	0.78	of free Cl came off.
" second hour . . .	0.54	" "
" third hour . . .	0.556	" "
" fourth hour . . .	0.487	" "

Total . . . 2.363

And at the same time 0.080 of HCl

Experiments on the Treatment of Silicates.—The treatment of silicates containing alkalis by chloride of calcium enables us to effect the extraction of these alkalis under conditions of high return and economical working that cannot be attained by any other process at present known. It further enables us to treat silicates—such as petalite—which are only attacked with difficulty by the usual reagents, with great ease, and to effect a veritable commercial analysis. The proportions of chloride of calcium and silicate to be used vary according to the composition of the silicate; the manner and duration of the heating have also a great influence on the success of the operation; but these conditions are easily arranged after a few laboratory trials. In this manner we change the alkalis into chlorides, using only a slight excess of chloride of calcium. A methodical washing with water removes all the chlorides, and they are easily dealt with afterwards. The residue insoluble in water—formed of silicate of

No.	Material and proportion.	Silica per cent of anhydrous silicate.	Total Cl given off.	Chlorine.		Lithia obtained per cent of silicate.
				Free.	As HCl .	
1.	$\text{CaCl}_2 + \text{Al}_2\text{O}_3$. .	0	7.37	88.2	11.8	—
	CaCl_2 Lepidolite.					
2.	1 : 1 . .	56.8	36.1	68.8	31.2	—
3.	1 : 1 . .	—	35.3	60	40	—
4.	1 : 2 . .	—	36.3	54.06	45.94	—
5.	1 : 2 . .	—	29	47	53	—
6.	1 : 2 . .	—	41.7	14.5	85.50	2.12
7.	1 : 2.57	—	47.3	38.6	61.40	1.45
8.	1 : 2 . .	—	38.6	—	—	2.10
9.	1 : 3 . .	—	50	43.8	56.2	0.92
10.	1 : 4 . .	—	60.2	35.25	64.75	0.77
11.	1 : 5 . .	—	58.1	30.29	69.71	0.46
	Moist kaolin.					
12.	1 : 1 . .	59.77	35.8	62.6	17.4	—
	Calcined kaolin.					
13.	1 : 1 . .	—	58.5	77.9	22.1	—
14.	1 : 2 . .	—	84.6	68.8	31.2	—
	Petalite.					
15.	1 : 1 . .	75	71	75.32	24.68	2.01
16.	1 : 2 . .	—	57.75	70.50	29.50	—
17.	1 : 2 . .	—	42.1	—	—	—
18.	1 : 3 . .	—	60.5	68.40	31.60	—
	Artificial anhydrous silicate of Al_2O_3 .					
19.	1 : 1.2	75	71.6	76.9	23.1	—
20.	$2\text{CaCl}_2 + \text{SiO}_2$. .	98	36.1	79.4	20.6	—
21.	$\text{CaCl}_2 + \text{SiO}_2$. .	98	62.3	81.6	18.4	—
22.	$\text{CaCl}_2 + \text{SiO}_2$. .	97	85	75.4	24.6	—
23.	$3\text{CaCl}_2 + 4\text{SiO}_2$. .	98	88	72.1	27.9	—
24.	$3\text{CaCl}_2 + 4\text{SiO}_2$. .	98	89.2	72.4	27.6	—
25.	$\text{CaCl}_2 + 2\text{SiO}_2$. .	98	89	74.9	25.1	—
26.	$\text{CaCl}_2 + 2\text{SiO}_2$. .	92	69.7	96.7	3.3	—
27.	$\text{CaCl}_2 + 3\text{SiO}_2$. .	98	89.5	82.6	17.4	—
28.	$\text{CaCl}_2 + 3\text{SiO}_2$. .	85	62.8	76	24	—
29.	$\text{CaCl}_2 : \text{SiO}_2$ 2 : 1	99	89.8	92.2	7.8	—
30.	$\text{CaCl}_2 : \text{SiO}_2$ 2 : 1	99	96.05	90.03	9.97	—

alumina and lime—is very easily attacked by HCl , with an abundant deposit of gelatinous silica. The magma thus obtained can be easily dried at 120° , owing to the CaCl_2 it contains, and gives an insoluble silica which remains, after being taken up with water acidulated with HCl , in the form of a dense easily washed sand. Finally, it suffices to evaporate the solution of CaCl_2 and Al_2Cl_6 obtained to dryness, and to heat the residue to 300° in a current of air to obtain, after washing with water, a very pure alumina, free from iron and lime, and very suitable for the manufacture of aluminium and its derivatives. The CaCl_2 can be used over again for the treatment of fresh quantities of silicates, or for making chlorine with the help of the very pure silica also obtained.

This method, applied to the treatment of lepidolite and petalite, which have already been used in the chlorine experiments, gave the following results, working on 100 grms. :—

Lepidolite.

Proportion: 2 Lepidolite to 1.5 Chloride of Calcium.
Time of Heating: Five hours at red heat.

	Obtained.	Theory.
Silica	53.00	54.5
Alumina	27.00	29.0
Chloride of potassium	14.14	14.20
Lithia	2.77	2.80

Or 97.1 per cent of the lithia present.

Petalite.

Proportion: 1 Petalite to 1 Chloride of Calcium.
Time of Heating: Five hours at red heat.

	Obtained.	Theory.
Silica	75.5	74.5
Alumina	17.0	20.75
Lithia.. .. .	2.30	2.30

Or 95.6 per cent of the lithia present.

Such returns are unobtainable by any other method in use up to the present time.—*Moniteur Scientifique*, Series 4, vol. xiv., April, 1900.

ON A

GAS OBTAINED FROM CYANOGEN WHICH APPEARS TO BE IDENTICAL WITH ARGON.

By Dr. T. L. PHIPSON.

WHEN dry cyanogen is passed into a glass tube heated to redness, and full of iron nails (*points de Paris*), devoid of rust, a gas is obtained which can be collected over water, in which liquid it is only slightly soluble. This gas is colourless, and almost odourless; it extinguishes a lighted match, without taking fire itself; it is not absorbed by potash, and when mixed with oxygen and submitted to the electric spark it does not detonate. 1000 c.c. weighed in two experiments 1.800 and 1.810 grms. at 0° C. and 30 inches barometer. These weighings were made with the best balance in my laboratory. This gas is therefore not nitrogen (of which 1000 c.c. in the same circumstances weigh 1.267 grms.), nor, *a fortiori*, cyanogen. It therefore contains carbon, and from these two determinations its atomic weight, or equivalent, would have the half of the quantity of carbon contained in cyanogen. It is perhaps identical with argon, of which about 1 per cent has been found in atmospheric air, and which would therefore be a carbide of nitrogen, containing half the carbon contained in cyanogen.

Laboratory of Analytical Chemistry,
Putney, S.W.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, May 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 184 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 2nd to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 184 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The drought recorded last month still continues, and was more accentuated during the latter half of the month, when only 0.08 inch of rain fell from the 13th to the 30th inclusive. The total rainfall at Oxford during April was 0.89 inch; the average is 1.66 inches, the deficiency is therefore 0.77 inch for the month. This reduces the excess for the year to 0.84 inch; at the present time the deficit is 11.8 per cent on the thirty years' average.

Our bacteriological examinations of 456 samples have given the results recorded in the following table; we have also examined 32 other samples, from special standpipes, &c., making 488 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 23 samples) ..	245
New River, filtered (mean of 101 samples) ..	4
Thames, unfiltered (mean of 23 samples) ..	955
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 251 samples)	10
Ditto ditto highest	118
Ditto ditto lowest	0
River Lea, unfiltered (mean of 23 samples) ..	324
River Lea, from the East London Company's clear-water wells (mean of 35 samples) ..	5

The results of the bacteriological examinations may be summed up in stating that the London supply during the month has been of very high microbial quality, and the results of the filtration highly satisfactory.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.*

By LILY G. KOLLOCK.
(Continued from p. 222).

MERCURY.

It is recorded (*Am. Chem. Journ.*, xi., 264) that mercury may be separated without difficulty with a low current and a large excess of alkaline cyanide. The deposits are noted as "compact, rather grey in colour, and showed in a few cases a drop-like nature so characteristic of mercury." The time required for the deposition under the conditions given was twelve to fourteen hours. Smith and Wallace (*Journ. Am. Chem. Soc.*, xvii., 612) published a number of separations of mercury from other metals—zinc, cadmium, cobalt, and nickel. The time required for separation was reduced to three and three and one-half hours.

In the experiments made this year the following conditions gave good results and confirmed those previously made:—A solution of mercuric chloride, containing 0.1439 gm. of mercury in 10 c.c. and five-tenths gm. of potassium cyanide, was diluted to 100 c.c. It was electrolysed with a current N.D.₁₀₀=0.07 A and V=3.2. The temperature of the solution was 65° C. In three hours the metal was completely deposited. The deposit was washed with slightly warm water (see Table X.).

The deposits obtained were light grey in colour and were easily washed. They were bright and metallic in appearance with higher voltage.

Separations.

Mercury from Copper.—Smith and Frankel (*Am. Chem. Journ.*, xi., 264) report the separation of mercury and

* Contribution from the John Harrison Laboratory of Chemistry, From the *Journal of the American Chemical Society*, xxi., No. 10.

TABLE X.

Mercury. Grm.	Potassium cyanide. Grm.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Mercury found. Grm.
0'1439	0'5	100	N.D. ₁₀₀ =0'07 A.	3'2	65°	3½	0'1441
0'1439	0'5	100	" =0'07 A.	3'2	65°	3½	0'1442
0'1439	0'5	100	" =0'02 A.	1'6	65°	6	0'1440
0'1439	0'5	100	" =0'07 A.	3'1	65°	3	0'1436

TABLE XI.

Mercury. Grm.	Copper. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Mercury found. Grm.
0'1216	0'1	2'0	125	N.D. ₁₀₀ =0'02 A.	1'09	Cold	16	0'1220
0'1216	0'1	2'5	125	" =0'03 A.	1'9	65°	4	0'1216
0'1216	0'15	3'5	125	" =0'035 A.	1'8	65°	2½	0'1213
0'1216	0'1	3'0	125	" =0'04 A.	1'9	65°	3	0'1215

TABLE XII.

Mercury. Grm.	Nickel. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Mercury found. Grm.
0'1216	0'1	2	125	N.D. ₁₀₀ =0'04 A.	1'7	65°	4	0'1220
0'1216	0'1	2	125	" =0'04 A.	2'2	65°	4	0'1220
0'1216	0'15	2'5	125	" =0'04 A.	2'2	65°	4	0'1211
0'1216	1	2	125	" =0'04 A.	2'2	65°	4	0'1213

TABLE XIII.

Mercury. Grm.	Cobalt. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Mercury deposited. Grm.
0'1216	0'1	2	100	N.D. ₁₀₀ =0'025 A.	2'45	Cold	16	0'1217
0'1216	0'1	2	100	" =0'025 A.	2'06	65°	5	0'1213
0'1158	0'1	2	100	" =0'03 A.	2'9	65°	5	0'1152

TABLE XIV.

Mercury. Grm.	Zinc. Grm.	Potassium cyanide. Grm.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Found. Grm.
0'1158	0'1	2	125	N.D. ₁₀₀ =0'05 A.	3	60°	4	0'1152
0'1158	0'1	1'5	125	" =0'033 A.	2'5	50°	4	0'1155
0'1158	0'2	2	125	" =0'025 A.	2'9	50°	4	0'1155

TABLE XV.

Mercury. Grm.	Platinum. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Mercury deposited. Grm.
0'1373	0'025	3	125	N.D. ₁₀₀ =0'05 A.	2'12	65°	4	0'1372
0'1373	0'01	3	125	" =0'04 A.	2'12	75°	4	0'1376
0'1373	0'01	3	125	" =0'045 A.	2'12	70°	4	0'1375

TABLE XVI.

Mercury. Grm.	Iron. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Mercury deposited. Grm.
0'1216	0'1	1	100	N.D. ₁₀₀ =0'05 A.	2	70°	3	0'1215
0'1216	0'3	3	100	" =0'04 A.	2	70°	4	0'1217
0'1216	2'5	2'5	100	" =0'02 A.	2'7	65°	4	0'1217

copper in an alkaline cyanide solution. A current generating 2 c.c. of oxyhydrogen gas per minute was used for this purpose. The solution used contained 0'1833 grm. of mercury and 14—70 per cent of copper was added. With a current generating 3½ c.c. of oxyhydrogen gas, mercury was completely deposited in sixteen hours. It is stated, however, that when the quantity of copper present exceeded 20 per cent the results were unsatisfactory. Later, Smith and McCauley took up the separation again, and by careful regulation of the current were enabled to effect it even when the metals were present in equal quantities.

In repeating this work, a solution of mercuric chloride equivalent to 0'1216 grm. of mercury and a copper sulphate solution equivalent to one-tenth grm. of copper were used. An excess of potassium cyanide was added. The entire solution was diluted to 125 c.c. The current acting upon the solution was N.D.₁₀₀=0'04 A and V=1'09. The temperature was 65°. In from two to four hours the

mercury was completely deposited. On testing the metal qualitatively the deposit was found free from copper (see Table XI).

Mercury from Nickel.—These metals were separated in an analogous manner to that described under the separation of silver from nickel. To the solutions of mercuric chloride and nickel nitrate were added 2 grms. of potassium cyanide. This was then diluted to 125 c.c. A current of N.D.₁₀₀=0'04 A and V=2'2 was allowed to act for three hours. The deposit was found to weigh 0'0003 grm. less than the calculated amount of mercury present. The filtrate was found to contain no mercury. No nickel was deposited with the metal (see Table XII.).

Mercury from Cobalt.—The mercuric chloride used in this separation contained 0'1216 grm. of mercury, and the cobalt nitrate contained one-tenth grm. of cobalt. Two grms. of potassium cyanide were added to the mixed solutions, which were diluted to 100 c.c. The current acting

was $N.D._{100}=0.03$ A and $V=2.9$. With a temperature of 60° the deposition of the mercury was complete in five hours. It was free from cobalt (see Table XIII.).

Mercury from Zinc.—The results obtained in the separation of mercury from zinc were first reported by Smith and Frankel in 1889. The electrolysis took place at the ordinary temperature in sixteen hours with a current generating 3 c.c. of oxyhydrogen gas per minute.

In the experiments made this year the following conditions gave satisfactory results (see Table XIV.).

In the third determination the current acted for three hours at 50° , and then all night in the cold. The deposit in all cases was grey and compact. The mercury on examination for zinc gave no reaction for that metal, while no mercury was found in the zinc solution.

Mercury from Cadmium.—As stated under the separation of silver from cadmium, Smith and Wallace (*Four. Am. Chem. Soc.*, xvii., 612) found that cadmium might be separated from both silver and mercury by keeping the temperature slightly elevated. Unless this precaution is taken, cadmium is precipitated with both metals, even when a low current is used.

The following proved to be good working conditions:—The mercuric chloride solution used contained 0.1182 gm. of mercury, and the cadmium sulphate solution was equivalent to 0.2206 gm. of cadmium. The double alkaline cyanides were produced by the addition of 24 grms. of potassium cyanide. A current of $N.D._{100}=0.018$ A and $V=1.7$ was passed through the solution, previously heated to 65° for seven hours. The mercury deposit was free from cadmium and weighed 0.1181 gm., which was 0.0001 gm. lighter than the theoretical amount of mercury. It was repeatedly found that when the current was greater than 0.02 A, cadmium was precipitated.

Mercury from Platinum.—This separation was first carried out and reported by Smith (*Am. Chem. Journ.*, xiii., 417). The deposit of mercury was effected by using a current generating 2 c.c. of oxyhydrogen gas a minute. The alkaline cyanide used for 0.1902 gm. of mercury was 24 grms. According to these suggestions a separation of the two metals was made. The mercury in solution was 0.1373 gm., and the platinum in the platonic chloride contained from 0.025 gm. to 0.1 gm. In four hours the separation was completed. The current was $N.D._{100}=0.05$ A and $V=2.1-2.3$. The results show an error of -0.0001 gm. to $+0.0003$ gm. (see Table XV.).

Mercury from Iron.—The separation of mercury from iron, like that of silver from iron, has not been previously attempted in alkaline cyanide solution. Accordingly the following method was developed and found to yield satisfactory results:—

The solution of the cyanide of iron was prepared from ferrous ammonium sulphate in precisely the same way as that described in the separation of silver from iron. The mercuric chloride solution contained 0.1216 gm. of mercury. The cyanide present was from 1 to 3 grms., and the current was $N.D._{100}=0.05$ A and $V=2.5$. The temperature during the electrolysis was maintained at 70° C. In three hours the mercury was completely deposited; it was free from iron. The mercury deposit was dissolved in concentrated nitric acid. After diluting, a few crystals of ammonium thiocyanate were added; a faint pink colour was observed, which was found to be due to the small trace of iron in the nitric acid (see Table XVI.).

(To be continued).

Detection of Glycerin.—L. Grunhut.—As the result of a number of comparative experiments, the author finds that there is but one certain method of detecting the presence of glycerin when it exists in only small quantities. A mixture of the substance under examination, and double its weight of SO_2KH , is made in a small flask: this is heated on a sand-bath; an escape-tube leads the fumes into a flask surrounded with a refrigerating mixture. If the substance contains glycerin the odour of acrolein is perceived very distinctly when cold.—*Zeit. Anal. Chem.*, xxxviii., p. 37.

ON THE PROGRESS OF CHEMISTRY IN GREAT BRITAIN AND IRELAND DURING THE NINETEENTH CENTURY.*

PART I.—FROM THE BEGINNING OF THE CENTURY TO THE FOUNDATION OF THE CHEMICAL SOCIETY (1841).

By T. E. THORPE, LL.D., F.R.S.,
President of the Chemical Society.

(Continued from p. 224).

THE promulgation of the atomic theory and the importation of the ideas of constancy of chemical composition and of definite numerical ratio, gave an immediate impetus to analytical chemistry, of which the operations were at length seen to be subject to a numerical check and control hitherto unknown and barely suspected. Whilst the reflecting goniometer, on the one hand, served to define the geometrical form of a substance, and to establish the constancy of that form with a precision unattainable by the graphometer of Carangeau, the balance, on the other, rendered more and more perfect, in response to the demands of the chemist upon the mechanic, in order to satisfy the conditions imposed by the fundamental laws of Dalton's hypothesis, served to determine its exact atomic composition. The first use to which Wollaston, in 1810, put his reflecting goniometer, was to measure with exactitude the primary angles of calc spar, the composition of which had been accurately ascertained by Richard Phillips in 1803. A number of compounds, indeed, had their real nature and composition established during this period, and in the light of the atomic theory. In fact, the memoir by Thomson on the Oxalates (*Phil. Trans.*, 1808), and that by Wollaston "On Super-acid and Sub-acid Salts" (*Phil. Trans.*, 1808), were of the greatest service as proving the validity of Dalton's theory of chemical combination. Smithson Tennant analysed emery. Hatchett ascertained the composition of magnetic pyrites; Chenevix that of the arseniates of copper and iron, and of bournonite; Thomson that of sodalite, fluor spar, and allanite.† Edward Clarke, of Cambridge, analysed petalite, gehlenite, the purple of Cassius, and examined the newly-discovered metal cadmium and its salts.

It would be impossible to exaggerate the influence which the discoveries of the first twenty years of the century exerted on the spirit of the age. They seemed, indeed, to presage a new era—the coming of a glorious day of which the dawn had already begun. No generalisation was more opportune in its announcement than that of Dalton; it was, indeed, to use the common phrase, "in the air." The teaching of a long succession of philosophers and the experimental labours of many workers had paved the way for its acceptance, and it is practically certain that had Dalton not formulated it, Wollaston or Berzelius would have done so. As it was, each of these distinguished men was almost immediately able to supply the strongest experimental proof of its soundness. Wollaston, from the outset, was well aware of the limitations of Dalton's explanation of the facts of chemical combination; and he recognised that the arithmetical relation alone of the proportions of elementary atoms is insufficient to explain their mutual action. As he says, "we shall be obliged to acquire a geometrical conception of their relative arrangement in all the three dimensions of solid extension." How Berzelius received the news of Dalton's discovery he has himself related in his memorable paper in *Gilbert's Journal*. This view of the combinations of bodies, he says, "appeared capable of illustrating so greatly the doctrine of affinity, that the confirmation of Dalton's hypothesis seemed to be the greatest step that chemistry, as a science, would have made during the whole time of its existence." How it was confirmed by Berzelius it is not

* Presidential Address to the Chemical Society, 1900.

† Allanite, in addition to cerium, contained, as he supposed, a new metal which he proposed to distinguish by the name of "junonium."

necessary here to state, nor need we set out in detail how the whole course of modern chemistry, however complex and many-sided it may seem, is really one vast elaboration of the atomic theory; in fact, as Liebig has said, all our ideas are so interwoven with that theory that it is difficult to carry ourselves back to the time when it did not exist. Dalton was the first recipient of one of the Royal medals which the Sovereign, on the recommendation of the Royal Society, annually bestows, and no more just award was ever made. Davy, in making known, as he said, "this first testimony of royal benevolence to science," stated that this discovery of the simple principle, universally applicable to the facts of chemistry, laid the foundations for future labours respecting the sublime and transcendental parts of the science of corpuscular motion. Dalton's merit, in this respect, resembles that of Kepler in astronomy. "The causes of chemical change are as yet unknown, and the laws by which they are governed; but in their connection with electrical and magnetic phenomena, there is a gleam of light pointing to a new dawn in science; and may we not hope that in another century, chemistry having, as it were, passed under the dominion of the mathematical sciences, may find some happy genius, similar in intellectual powers to the highest and immortal ornament of this Society, capable of unfolding its wonderful and mysterious laws."

Volta's famous letter of March 20th, 1800, to Sir Joseph Banks, was as the "order of the day" of a great leader. No more momentous document was ever given to the scientific world. "The voltaic battery," said Davy, in one of his characteristically happy phrases, "was as an alarm-bell to experimenters in every part of Europe; and it served no less for demonstrating new properties in electricity, and for establishing the laws of this science, than as an instrument of discovery in other branches of knowledge; exhibiting relations between subjects before apparently without connection, and serving as a bond of unity between chemical and physical philosophy."

It is not necessary here to dilate upon what this "instrument of discovery" in the hands of our countrymen has done for the development of chemistry. April 30th, 1800, when Nicholson and Carlisle first effected the decomposition of water by electrolysis, is a red-letter day in the history of our science. The *Transactions of the Royal Society*, *Nicholson's Journal*, and the *Philosophical Magazine* in the first years of the century show with what ardour and with what a lively expectancy "the new galvanic apparatus of Mr. Volta" was applied.*

Although even as far into the century as the date of Waterloo, the theory of the compound nature of water was regarded by some as "nothing more than a fanciful conjecture" and "a bare assertion without any proof whatever," there can be no question that Nicholson and Carlisle's discovery was of the greatest service in affording what was then, and long subsequently, looked upon as one of the strongest analytical proofs of the validity of the fact. But in their effect upon the popular imagination, these discoveries altogether paled before that of Davy. The isolation of potassium is, in reality, one of the most dramatic episodes of an epoch fruitful in striking incidents. The remarkable nature of the substance itself, its intense chemical activity, its significant chemical relationships, and the astonishing and far-reaching possibilities which its very existence seemed to open out, were all calculated to impress the minds of *virtuosi* and vulgar alike. Davy's triumph, indeed, was regarded as the realisation of a confident anticipation that the most important discoveries in chemistry were about to be made by the help of galvanism—an anticipation which found expression in almost every issue of the scientific journals of the time. There is little wonder, therefore, that a

succession of scientific events of such magnitude as those which characterised the opening years of this century should have powerfully excited the imaginations of all cultured persons, and that optimists in every country, under the sway of ideas which made up the social and political philosophy of the time, should look forward in sure and certain hope in the immediate advent of a new era—to the coming of a generated humanity in a golden age. Thus Christopher Girtanner, of Göttingen, whose name lives only in connection with the fact that he was the first German chemist to appreciate and teach the new doctrines of the French School, was convinced that in the 19th century the transmutation of the metals would be generally known and practised. "Every chemist," he says, "every artist, will make gold; kitchen utensils will be of silver, and even gold. . . . There will be no other riches than natural riches—the productions of the soil; artificial riches, such as gold, silver, and paper money, will vanish in the hands of those who have accumulated them. What a revolution in society! Every enlightened chemist, however, will agree with me that this revolution is not only probable, but at no great distance." Unhappily for Dr. Girtanner's reputation as a prophet, the social revolution he foretold may not be reckoned among the achievements of the 19th century. Enlightened chemists still appear to have an eye to artificial riches, not scorning even paper money; and although, unfortunately, the precious metals do occasionally vanish in our hands, it is not because we convert them into kitchen utensils.

Even the sober-minded Faraday was not insensible to the visions thus created. In the course of his lectures on the metals, given in 1818 to the City Philosophical Society, he says, "to decompose the metals, then to re-form them, to change them from one to another, and to realise the once absurd notion of transmutation, are the problems now given to the chemist for solution. Let none start at the difficult task, and think the means far beyond them. Let us but look to the means which have given us these bodies, and to their gradual development, and we shall then gain confidence to hope for new and effective powers for their removal from the elementary ranks. . . . Consider the improvement when, by a variety of manipulations, the early chemist of the last century separated a small quantity of a metallic substance from five or six other bodies, where it existed in strong combination, and then passed to the perfection of these means as exhibited in the admirable researches of Tennant and Wollaston; lastly, glance but at the new, the extraordinary powers which the chemist of our own nation put in action so successfully for the reduction of the alkalis and earths, and you will then no longer doubt that powers still progressive and advanced may exist and put at some favourable moment the bases of the metals in our hands."

It is interesting to note that, even as far back as 1806, an effort was made to form a Chemical Society independent of the Royal Society, to be called the London Chemical Society, but it received scant encouragement from persons in high places, and few chemists of note joined its ranks. Sir Joseph Banks, indeed, frowned down upon all such attempts. "I see plainly," he once said, "that all these new-fangled associations will finally dismantle the Royal Society, and not leave the old lady a rag to cover her." And the frown of the masterful old President meant social ostracism to all who chose to disregard it. But, unlike his predecessor, Sir John Pringle, who, on a certain memorable occasion, confessed to George III. that he was unable to reverse the laws and operations of nature, and was then told he had better resign, Banks, if he could not reverse, could at least control and modify a natural tendency, and with the aid of Wollaston, Davy, Hatchett, and Brande, he managed to keep chemistry for a time almost exclusively under the cloak of "the old lady."

Priestley died on February 9th, 1804. Although he

* This at the time was usually constructed of plates of silver and zinc, with intervening pieces of cloth. "Most of our philosophers," we are told, "have used half-crowns for the silver plates," and zinc could be bought at 8d. per lb. at the White Lion in Foster Lane, and cast in moulds of chalk.

lived long enough to have read of Dalton's explanation of the laws of chemical combination, as explained in Thomson's "System," and although he must have heard of the electrolytic decomposition of water by Nicholson and Carlisle in 1800, nothing apparently could shake his conviction of the essential and inherent truth of the conception of phlogiston. The last of his published writings was his memoir on "The Doctrine of Phlogiston established, and that of the Composition of Water refuted." Tolerant and receptive as he was in all other matters of opinion, and especially in matters of religious belief, he seemed utterly incapable of appreciating the real significance of the rapidly accumulating mass of facts, or of drawing any correct inferences from them.

Cavendish, "le plus riche de tous les savans et probablement aussi le plus savant de tous les riches," died in 1810. His work belongs to a preceding age, for on the downfall of phlogistonism he had ceased to occupy himself with chemical pursuits, and it must ever remain doubtful how far he gave in his adhesion to the new doctrine to which his own cardinal discovery so largely contributed.

In the year 1815 appeared Thomson's *Annals of Philosophy* (vi., 321), an anonymous essay "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," which the author states he submits "to the public with the greatest diffidence; for, although he has taken the utmost pains to arrive at the truth, yet he has not that confidence in his abilities as an experimentalist as to induce him to dictate to others far superior to himself in chemical acquirements and fame." With this modest preamble the author proceeds to discuss certain consequences which seem to him to follow from the doctrine of volumes at first generalised by Gay-Lussac. The paper is remarkable, in spite of its errors and crudities, for its originality and lucidity. Its author was eventually discovered to be William Prout, then a young medical student, who lived to become eminent as a physiological chemist. His work thus tentatively put forward has become classical as containing, or rather suggesting, the hypothesis that the atomic weights of the elements are multiples of that of hydrogen. For it is noteworthy that the paper nowhere contains in explicit terms the statement of what is now known as Prout's law. Its main purpose was to set out more clearly than had hitherto been perceived the relation between the doctrine of gaseous volumes and of atoms, and it is only incidentally remarked that he "had often observed the near approach to round numbers of many of the weights of the atoms," and that "Dr. Thomson appears to have made the same remark." He further points out that it would appear from his tables "that all elementary numbers, hydrogen being considered as 1, are divisible by 4, except carbon, azote, and barytium, and these are divisible by 2, appearing, therefore, to indicate that they are modified by a higher number than that of unity or hydrogen. Is the other number 16 or oxygen? And are all substances compounded of these two elements?" Prout's "law" has been frequently so stated as to imply that all substances are "compounded" of hydrogen. But, as will be seen, his own words convey no such idea.

It is not improbable that the idea that all atomic weights were actually integers would have attracted little, if any, attention, had it not been adopted by Thomson and given currency by means of his "System of Chemistry," then, and for some years subsequently, one of the leading British text-books.

Smithson Tennant, Professor of Chemistry in the University of Cambridge, a man of whom it was said, in Johnson's well-known words, is "to be mentioned with reverence rather for the possession than the exertion of uncommon abilities," died in 1815—accidentally killed whilst riding in the neighbourhood of Boulogne. Born at Selby, in 1761, and a pupil of Black, he was early attracted to the study of chemistry, which he continued to prosecute at Cambridge as a Fellow Commoner of Christ's

College. His private fortune exempted him from the necessity of following actively any profession. Although a man of wide reading, and of a quick and active mind, we are told that there was a singular air of carelessness and indifference in his habits and mode of life, his manners, appearance, and conversation being the most remote from those of a professed student. "His college rooms exhibited a strange, disorderly appearance of books, papers, and implements of chemistry, piled up in heaps, or thrown in confusion together." He was fond of foreign travel, and, in the course of one of his journeys, made the acquaintance of Scheele, for whom he had a high admiration. He was also on terms of friendship with many of the leading French chemists of his time. Chemistry in Germany at this period was a mixture of science and credulity, the philosopher's stone was spoken of with respect, and Tennant relates that he received from a man of science and character an introduction to a person who was reputed to be in possession of that treasure, with whom he conversed in Latin, and who exhibited to him the mysterious powder "enlarging upon its transcendent qualities with much pomp, and in flowing and sonorous periods."

Tennant is best known for his analysis of carbon dioxide, his work on the nature of the diamond, and on the injurious effects of magnesia in agriculture, his chemical examination of emery, and his discovery of iridium—so named from the various colours of its solutions, and osmium—which owes its name to the smell of certain of its oxides. In the course of an inquiry by a Committee of the Royal Society, formed at the request of the Government to investigate the danger that might attend the general introduction of gas lighting in the metropolis, he made the observation that flame will not pass through small tubes, a discovery which in the hands of Davy led to the invention of the safety lamp.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 3rd, 1900.

Professor THORPE, F.R.S., President, in the Chair.

A BALLOT for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. Alexander William Bain, B.A., Heinrich Rowland Beringer, Frank Curzon Britten, B.A., John Richard Brooke, A.I.C., Arthur Brand Chater, Nicholas Cullinan, M.D., John Cussons, B.Sc., Arthur Charles Davis, Noël Fielding Deerr, William Donald, Robert Eadie, Frederic Richard Ellis, Thomas FitzGibbon, Morris Broad Fowler, Reginald Gordon Halstead, James Herbert Haines, B.Sc., Henry Jennings, James Henry Kershaw, Adolf Liebmann, M.A., Ph.D., Thomas Lamb Lockhart, Thomas Macara, Frederick Thomas Munton, Robert Pettigrew, Geoffrey Surtees Phillpotts, B.A., James Wallace Sandford, Bertram D. Steele, B.Sc., James Walter Tilley, Augustus John Walker, B.Sc.

Certificates were read for the first time in favour of Messrs. George Edward Battle, Totlands, Dane Park, Ramsgate; John Henry Gough, 22, Francis Street, Chapel-town Road, Leeds; Percy John Hinks, 16, Moreton Road, South Croydon; Tajiro Ichioka, 8, Nottingham Place, London; David Herbert Patrick, Earlsdon, Coventry; Timothy A. Smiddy, Kilbarry House, Cork, Ireland.

Of the following papers, those marked * were read:—

*61. "The Substituted Nitrogen Chlorides and Nitrogen Bromides Derived from Ortho- and Para-acet-toluids." By F. D. CHATTAWAY and K. J. P. ORTON.

Both *o*- and *p*-acet-toluide when treated with hypochlorous or hypobromous acid, produce nitrogen chlorides and bromides, which readily undergo transformation into the isomeric substituted toluides; these in their turn form nitrogen chlorides and bromides, which pass into the disubstituted toluides, in which the amino-hydrogen is again replaceable by chlorine or bromine. As with the substituted anilides, when the ortho- and para-positions relatively to the acetamino-group are occupied, the compounds undergo no further isomeric change, hydrolysis, or decomposition resulting from attempts to induce it.

The halogen, exactly as in the case of acetanilide or a substituted acetanilide, is found always to take up the para-position when this is possible, and when this position is occupied, the ortho-position, relatively to the carbon to which the nitrogen is attached. The authors have shown (*Trans.*, 1899, lxxv., 1046; 1900, lxxvii., 134; *Ber.*, 1899, xxxii., 3573), that substitution by chlorine or bromine in anilines and anilides is not a direct process, but a result of the transformation of a nitrogen chloride or bromide, a hypochlorite or hypobromite being probably formed first by the nitrogen becoming quinquivalent. The behaviour of the nitrogen chlorides and bromides derived from the toluides is in entire agreement with this conclusion.

The properties of the nitrogen chlorides and bromides obtained from the toluides resemble exactly those of other members of the class. The nitrogen chlorides are colourless, the nitrogen bromides sulphur-yellow solids, all crystallising well in four-sided prisms terminated by domes.

All show the general reactions of nitrogen chlorides and bromides. They react with alcohol, re-forming the toluide and producing ethyl hypochlorite or hypobromite, although this action is usually accompanied by a considerable amount of isomeric change.

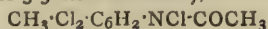
They react with ammonia liberating nitrogen, with hydrocyanic acid forming cyanogen chloride or bromide, with hydrogen chloride, bromide, or iodide setting free the halogen, and with hydrogen peroxide oxygen, in each case the toluide being re-formed. On warming with dilute acids, a certain amount of hydrolysis accompanies the isomeric change, and this, in the case of the nitrogen bromides, is the chief action.

The following compounds are described:—

o-Methyl-phenyl-acetyl-nitrogen chloride (ortho-acet-chloramino-toluene), $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NCl}\cdot\text{COCH}_3$, m. p. 43°.

Methyl-chlor-phenyl-acetyl-nitrogen chloride (ortho-acet-chloramino-5-chlor-toluene), $\text{CH}_3\cdot\text{Cl}\cdot\text{C}_6\text{H}_3\cdot\text{NCl}\cdot\text{COCH}_3$ (Me: Cl: : 2: 4), m. p. 66°.

Methyl-dichlor-phenyl-acetyl-nitrogen chloride (ortho-acet-chloramino-3: 5-dichlor-toluene),—

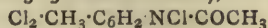


(Me: Cl: Cl: : 2: 4: 6), m. p. 78°.

p-Methyl-phenyl-acetyl-nitrogen chloride (para-acet-chloramino-toluene), $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NCl}\cdot\text{COCH}_3$, m. p. 91–92°.

Methyl-chlor-phenyl-acetyl nitrogen chloride (para-acet-chloramino-3-chlor-toluene), $\text{CH}_3\cdot\text{Cl}\cdot\text{C}_6\text{H}_3\cdot\text{NCl}\cdot\text{COCH}_3$ (Me: Cl: : 4: 2), m. p. 48°.

Methyl-dichlor-phenyl-acetyl nitrogen chloride (para-acet-chloramino-3: 5-dichlor-toluene),—

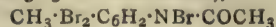


(Me: Cl: Cl: : 4: 2: 6), m. p. 72°.

o-Methyl-phenyl-acetyl-nitrogen bromide (ortho-acet-bromamino-toluene), $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NBr}\cdot\text{COCH}_3$, m. p. 100.5°.

Methyl-brom-phenyl-acetyl-nitrogen bromide (ortho-acet-bromamino-5-brom-toluene), $\text{CH}_3\cdot\text{Br}\cdot\text{C}_6\text{H}_3\cdot\text{NBr}\cdot\text{COCH}_3$ (Me: Br: : 2: 4), m. p. 91°.

Methyl dibrom-phenyl-acetyl-nitrogen bromide (ortho-acet-bromamino-3: 5-dibromotoluene),—



(Me: Br: Br: : 2: 4: 6), m. p. 120°.

p-Methyl-phenyl-acetyl-nitrogen bromide (para-acet-bromamino-toluene), $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NBr}\cdot\text{COCH}_3$, m. p. 64–95°.

Methyl-brom-phenyl-acetyl-nitrogen bromide (para-acet-bromamino-3-brom-toluene), $\text{Br}\cdot\text{CH}_3\cdot\text{C}_6\text{H}_3\cdot\text{NBr}\cdot\text{COCH}_3$ (Me: Br: : 4: 2), m. p. 87°.

Methyl-dibrom-phenyl-acetyl-nitrogen bromide (para-acet-bromamino-3: 5-dibromo-toluene),—
 $\text{Br}_2\cdot\text{CH}_3\cdot\text{C}_6\text{H}_2\cdot\text{NBr}\cdot\text{COCH}_3$
(Me: Br: Br: : 4: 2: 6), m. p. 118°.

*62. "The Estimation of Hypoiodites and Iodates; and the Reaction of Iodine Monochloride with Alkalis." By K. J. P. ORTON and W. L. BLACKMAN.

The method of estimating hypoiodites is based on the oxidation of sodium arsenite by hypoiodites, but not by iodates. Excess of the standard arsenite is used, and the unoxidised portion titrated with iodine after the saturation of the alkali by carbon dioxide. The iodate can then be determined by acidifying and titrating the iodine liberated. The hypoiodite solutions were prepared chiefly from iodine monochloride (dissolved in hydrochloric acid), and also from iodine solution. The initial reaction of iodine monochloride and alkalis is represented by the equation $\text{ICl} + 2\text{MOH} = \text{MIO} + \text{MCl} + \text{H}_2\text{O}$.

With potash, soda, lime-water, and baryta water, the whole of the iodine is for a short time (varying from thirty seconds to five minutes) present as hypoiodite. The transformation into iodate and iodide is practically complete after twenty-four hours. With ammonia, the complete transformation requires two or three weeks. The solution obtained from methylamine and iodine monochloride behaves in an exceptional manner, the hypoiodite gradually disappearing, probably oxidising the methylamine. The bleaching of indigo is shown to be unsuitable for the purpose of estimating hypoiodites, owing to the direct action of even dilute alkalis on the indigo.

The solutions obtained by shaking up iodine with mercuric oxide and water contain chiefly iodate, and only a small quantity of hypoiodite.

DISCUSSION.

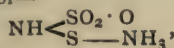
In reply to the President, Dr. ORTON said that the work of which he had given an account was complete in fifteen months before the abstract of R. L. Taylor's paper (*Proc.*, 1900, xvi., 70) appeared.

*63. "Products of the Action of Sulphur Dioxide on Ammonia." By EDWARD DIVERS.

When the paper on "Ammonium Amidosulphite" (Divers and Ogawa, *Proc.*, 1900, xvi., 38; *Trans.*, 1900, lxxvii., 327) was communicated to the Society, the authors were unaware that a paper on the subject of this note had been published by Schumann (*Zeit. Anorg. Chim.*, 1900, xxi., 43). Beyond the fact that Schumann also points out the incorrectness of Rose's statement that sulphur dioxide combines with only its own volume of ammonia, the two papers have nothing in common. The main fact established in the paper by Ogawa and the author was the existence of ammonium amidosulphite, of which they had already given notice in a paper on "Ethyl Ammoniumsulphite" (*Trans.*, 1899, lxxv., 534). Schumann has obtained a product of the same composition as ammonium amidosulphite in red masses, not very hygroscopic; it dissolves in water to a yellow solution, forming ammonium sulphate, sulphite, thiosulphate, trithionate, and pentathionate, whilst ammonium sulphite is a white, crystalline powder extremely deliquescent, and soluble in water, forming ammonium sulphite only. Schumann obtained two other products, having respectively the formulæ $\text{SO}_2\cdot\text{NH}_3$ and $3\text{SO}_2\cdot\text{NH}_3$, the aqueous solutions of which were similar to that given by the red substance $\text{SO}_2\cdot\text{NH}_3$. The author can only regard Schumann's three products as mixtures of substances formed by the spontaneous decomposition of ammonium amidosulphite.

Since the publication of the paper on ammonium amidosulphite, further work by Ogawa has fully established

the existence amongst the products of the decomposition of this salt of the compound formulated (*loc. cit.*, p. 334) as $(\text{NH}_3)_2\text{S}_2\text{O}_3$, but of which the true formula is $\text{N}_2\text{H}_4\text{S}_2\text{O}_3$. Although only faintly acid to litmus, it forms salts, of which the ammonium salt, $\text{NH}_4\text{N}_2\text{H}_3\text{S}_2\text{O}_3$, the potassium salt, $\text{KN}_2\text{H}_3\text{S}_2\text{O}_3$, the barium salt, $\text{Ba}(\text{N}_2\text{H}_3\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$, and the lead salt, $\text{Pb}(\text{N}_2\text{H}_3\text{S}_2\text{O}_3)_2$, have been prepared. The constitutional formula $\text{NH}_2\text{S}\cdot\text{NH}\cdot\text{SO}_3\text{H}$, or—

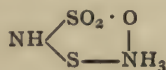


seems to express the relations of this substance as far as they are at present known.

This preliminary notice is published because, unfortunately, the circumstances in which the author and Ogawa are placed afford little hope of the full account of the products of the decomposition of ammonium amidosulphite being ready for publication for some considerable time to come.

DISCUSSION.

Dr. TRAVERS asked if the author attributed the formula—



to the compound he had described merely from analogy with amidoacetic acid.

Dr. HEWETT asked whether any decomposition products of the compound $\text{N}_2\text{H}_4\text{S}_2\text{O}_3$ had been obtained in which the sulphur and nitrogen were still linked together. There seemed to be a possibility of isolating the sulphur analogue of hydroxylamine, or some compound nearly related to it.

Dr. DIVERS replied that this substance hydrolysed as a sulphonic acid, and yet was not acid to litmus like all other sulphonic acids. The red substance soluble in carbon disulphide and ether might well be the sulphur amide, $\text{S}(\text{NH}_2)_2$, supposed to exist by Forchhammer.

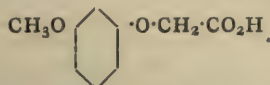
64. "On Brazilin." IV. By A. W. GILBODY, W. H. PERKIN, jun., and J. YATES.

In a previous communication (*Proc.*, 1899, xv., 27), it was shown that trimethylbrazilin, $\text{OH}\cdot\text{C}_{16}\text{H}_{10}\text{O}(\text{OCH}_3)_3$, when oxidised with chromic acid, is converted into trimethylbrazilone, $\text{OH}\cdot\text{C}_{16}\text{H}_8\text{O}_2(\text{OCH}_3)_3$, and that this substance when heated loses water, with formation of dehydrotrimethylbrazilone, $\text{OH}\cdot\text{C}_{16}\text{H}_6\text{O}(\text{OCH}_3)_3$, a compound which yields an acetyl derivative, and which is evidently identical with the acetyl compound which Herzog prepared by the oxidation of acetyltrimethylbrazilin (*Monatshfte.*, 1895, xvi., 913). The authors now find that trimethylbrazilone, on treatment with phenylhydrazine, is reduced to a substance having the formula $\text{C}_{19}\text{H}_{18}\text{O}_4$, which melts at 173° , and dissolves in nitric acid and other concentrated mineral acids, yielding intense purple or orange solutions.

When trimethylbrazilin is oxidised with potassium permanganate under various conditions, a variety of substances are formed, the principal of which are the following:—

(1). A dibasic acid, $\text{C}_{10}\text{H}_{10}\text{O}_6$, melting at 175° . This acid contains one methoxyl group, and is derived from the resorcinol portion of the molecule of brazilin, because, when fused with potash, it yields a substance which gives an intense violet colouration with ferric chloride.

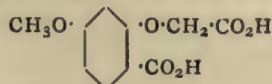
When heated with water at 200° , this acid, $\text{C}_{10}\text{H}_{10}\text{O}_6$, is decomposed, with elimination of carbonic anhydride and formation of a monobasic acid, $\text{C}_9\text{H}_{10}\text{O}_4$ (m. p. 119°), which has been shown by synthesis to have the constitution—



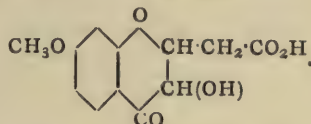
In synthesising this acid, for which the name *methyl-resorcinolacetic acid* is proposed, pure methylresorcinol,

$\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, was treated with sodium ethoxide and ethyl bromacetate, and in this way *ethyl-methylresorcinol-acetate*, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, was obtained as a thick, colourless oil boiling at 182° (25 m.m.); this, on hydrolysis, yielded the corresponding acid which melted at 119° , and was found to be identical with the acid $\text{C}_9\text{H}_{10}\text{O}_4$, obtained from brazilin as described above.

Since brazilin under other conditions (see below, and *Proc.*, 1899, xv., 27–29) yields *p*-methoxy-salicylic acid it follows that the acid, $\text{C}_{10}\text{H}_{10}\text{O}_6$, must be the *methyl-carboxyresorcylic acid* having the formula—



(2). A monobasic acid, $\text{C}_{10}\text{H}_8\text{O}_5(\text{OCH}_3)\cdot\text{CO}_2\text{H}$, melting at 129.5° , which has already been described (*Proc.*, 1899, xv., 29). We find that this acid, when treated with concentrated sulphuric acid at 80° , loses water, and is converted into an acid, $\text{C}_{12}\text{H}_{10}\text{O}_5$, which melts at 196° , and when oxidised with permanganate yields *p*-methoxy-salicylic acid. It is therefore probable that the acid, $\text{C}_{10}\text{H}_8\text{O}_5(\text{OCH}_3)\cdot\text{CO}_2\text{H}$, has the constitution—



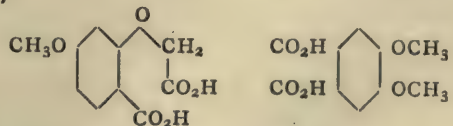
(3). An acid very sparingly soluble in water and melting at 208° . This acid has the formula $\text{C}_{19}\text{H}_{18}\text{O}_9$; it yields a silver salt $\text{C}_{17}\text{H}_{16}\text{O}_5(\text{CO}_2\text{Ag})_2$, and a dimethyl salt, $\text{C}_{17}\text{H}_{16}\text{O}_5(\text{CO}_2\text{Me})_2$ (m. p. 110°), and is therefore dibasic. When fused with potash, it yields a substance soluble in water, which, with ferric chloride, gives an intense catechol reaction; it does not form an oxime, but when reduced with sodium amalgam, it is converted into an acid, $\text{C}_{17}\text{H}_{16}\text{O}_4(\text{CO}_2\text{H})_2$, which melts at 227° .

When the acid $\text{C}_{17}\text{H}_{16}\text{O}_5(\text{CO}_2\text{H})_2$ is heated at 140° with alcoholic potash, it is decomposed with formation of a neutral substance, the analysis of which agrees better with the formula $\text{C}_{17}\text{H}_{20}\text{O}_5$ than with $\text{C}_{17}\text{H}_{18}\text{O}_5$; it appears probable therefore that, besides elimination of carbonic anhydride, reduction has taken place according to the equation $\text{C}_{17}\text{H}_{16}\text{O}_5(\text{CO}_2\text{H})_2 + 2\text{H} = \text{C}_{17}\text{H}_{20}\text{O}_5 + 2\text{CO}_2$. This substance crystallises from alcohol in needles, melts at 140° , and appears to be a lactone.

(4). An acid very sparingly soluble in water, which melts at $214\text{--}215^\circ$ with vigorous decomposition, and gives also an intense catechol reaction after fusion with potash and treatment with ferric chloride. The results of one analysis point to this acid having the formula $\text{C}_{13}\text{H}_{14}\text{O}_8$, but, unfortunately, it has so far been obtained in such small quantity that the analysis could not be repeated.

(5). Metahemipinic acid.

Constitution of Brazilin.—The results described in this and previous communications, and especially the isolation of methylcarboxyresorcylic acid and of metahemipinic acid,—



from among the products of the oxidation of the brazilin, allow of only a very few formulæ as possible expressions of the constitution of this substance, and after carefully considering all the facts, the authors are of the opinion that brazilin probably has the constitution represented by the formula,—

Dr. LEHFELDT called attention to some experiments which had been performed to measure the potential difference between an electrolyte and a gas. The electrolytes considered were chiefly aqueous solutions, and the potential differences observed varied largely. The surface tensions of the liquids were measured, and it was shown that the variations in the potential difference were very similar to those in surface tension. This suggests, in the case of electrolytes, true physical surface effects, and not chemical action.

The CHAIRMAN remarked that Dr. Lehfeltdt evidently looked upon the metal-ether boundary as being the effective one. The experimental evidence is not sufficient to say exactly which is the effective contact, but it seems to show that the metal-ether effect is of the same order of magnitude as the oxygen layer effect. According to Helmholtz they ought to be related, and they apparently are.

The CHAIRMAN then read a paper by Mr. J. B. TAYLER on "*The Heat of Formation of Alloys.*"

Experiments have been made upon alloys of lead with tin, bismuth, and zinc, and of zinc with tin and mercury. The method employed consisted in dissolving (1) the alloy, and (2) the corresponding mixture of metals in mercury and measuring the heat of solution in each case. On the assumption that the solutions obtained are identical, the difference between the heat of solution of the mixture and that of the alloy is the heat of formation of the latter. The calorimeter was a thin glass tube silvered on the outside, and supported by a stouter tube silvered on the inside. Suitable arrangements were adopted for the introduction of the metals or alloys, which were used in the form of filings. Solution was often complete in less than a minute, and rarely took more than two minutes and a half. The alloys first experimented upon contained their constituents in equivalent proportions, and the heats of formation were found to be small in comparison with those found for brass by Galt and Baker. It was thought that only a small percentage of the atoms present had entered into definite chemical combination, and that more reliable results would be obtained by dissolving a small quantity of one metal in an excess of the other, and calculating from the experimental results the heat of formation of the grm.-molecular weight of compound upon the supposition that the whole of the small quantity of metal had entered into chemical combination by the exercise of its normal valency. Using the numbers so obtained to find, by Kelvin's theory, the potential difference which should exist between the metals concerned when put in contact, results were arrived at which agreed neither with the Volta effect or the Peltier effect, but which were considerably nearer the former than the latter.

A paper on "*The Want of Uniformity in the Action of Copper-zinc Alloys on Nitric Acid*" was read by Dr. J. H. GLADSTONE.

Experiments have been made by dissolving copper-zinc alloys in nitric acid, following the method of Dr. Galt, and adopting the precautions mentioned by him. The reaction between nitric acid and these metals or alloys is very complicated, and there is a difference between the products in the case of an alloy and in the case of the equivalent mixed metals. The gases evolved being small in the experiments performed, attention was directed to the determination of the substances remaining in solution, i.e., the nitrous acid and ammonia. The alloys gave much more nitrous acid and less ammonia; in fact, two of the alloys employed produced no ammonia. Discrepancies in results may be due to the fact that the zinc and copper in contact form a zinc-copper couple, which in the presence of acid sets up a vigorous action, and produces a different evolution of heat. Difficulties arise in the investigation because the alloys used may not be definite chemical compounds, but mixtures of two or more alloys with uncombined zinc and copper. The alloy with 38.38 per cent

of copper appears to be fairly uniform. Different observers disagree as to the amount of heat produced by any reaction, but the excess of calories in a zinc reaction over those in a copper reaction appears to be fairly constant. Starting with 640 calories, the value, according to Galt, when copper is dissolved in nitric acid of sp. gr. 1.360, we should have 1357 calories when zinc is dissolved, provided the chemical action is the same in each case. All the calorimetric results from the different specimens of alloys would theoretically lie upon the straight line drawn between 604 and 1357. This is practically so from pure copper to the copper 70 per cent alloy, but beyond that there is less heat produced than that indicated by the straight line law, the maximum deviation lying at about copper 37 per cent. The specimen containing 38.38 per cent copper, which is not far from the alloy CuZn_2 , shows a loss of 32 calories. The only way in which this deficit can be accounted for is by supposing that the action of this alloy on nitric acid produces a larger quantity of nitric oxide than in the case of pure copper. But allowing full force to this argument it cannot account for as much as 10 calories of the deficit. There is therefore a residual deficit as yet unaccounted for on chemical grounds. The author states that it is desirable that experiments should be conducted on the zinc-copper alloys with solvents which give a simpler chemical action than that produced by nitric acid.

The CHAIRMAN pointed out that the results obtained by Galt for an alloy which appeared to be a chemical compound were in close agreement with what would be expected from the existence of the Volta contact force.

Prof. ARMSTRONG said that the action of nitric acid on brass or zinc and copper was a function of the quantity of acid present, its strength, the temperature, and the pressure, and that therefore it was unsatisfactory to conduct experiments using nitric acid as a solvent. He suggested the use of a solution of bromine, in which finely powdered zinc, copper, and brass are easily soluble with a simple chemical reaction.

Mr. TOMLINSON pointed out that it was impossible to use the ordinary formula for the calculation of the Volta effect from the heat of formation of alloys, unless we know exactly the chemical composition of the alloy which is produced.

Mr. W. R. COOPER, referring to Mr. Tayler's paper, said that it was difficult to see that anything could be proved by the application of the Kelvin theory to a metallic contact unless there is ground for believing that some particular alloy of fixed composition is always formed. There is also a further difficulty in converting heat of formation into E.M.F. in cases where the metals have different valencies, for there is no reason why one valency should be selected rather than the other. Referring to Dr. Gladstone's paper, Mr. COOPER said that it was possible that the difference in the reducing powers of mixtures and alloys might be due to local action, which would be more pronounced in the case of alloys. More hydrogen would be evolved, and the reduction would be more complete.

Prof. S. P. THOMPSON then showed an Electromagnetic Experiment. A circular coil, capable of carrying a strong current, was placed with its axis horizontal in a tank of water. Into the tank were also placed some small magnets in sealed glass tubes, so adjusted as to have a density approximately equal to that of water. The magnets just floated or just sank. On running a current through the coil it was possible to "fish" for the magnets, which, acted upon by the magnetic field, immediately made their way to the coil. When the current was carefully reversed upon the approach of a magnet, repulsion instead of attraction took place, and the magnet retreated. In general, however, reversal of the current produced reversed polarity in the magnet, and attraction still persisted.

The Society then adjourned until May 25th.

CORRESPONDENCE.

DETERMINATION OF NICKEL IN NICKEL STEEL.

To the Editor of the Chemical News.

SIR,—Although Mr. Sargent in his paper on "The Determination of Nickel in Nickel Steel" (CHEM. NEWS, lxxxii., p. 209) standardises the potassium cyanide with the *nitrate* of nickel, he remarks later that "the titration may be accomplished in the presence of most all the salts of ammonium and the fixed alkalis *except the nitrates*."

The titration Mr. Sargent employs is very extensively used under the impression that alkaline nitrates exert no appreciable influence; if that impression does not correspond with actual fact, for ammonium nitrate at least, then many others besides myself have frequently returned inaccurate results.

To remove the uncertainty which Mr. Sargent's assertion originates I have titrated 0.05 gm. of nickel in the presence of varying amounts of the undermentioned alkali nitrates. The figures (c.c. KCN) used show that nitrates do not interfere at all.

Cryst. nitrate of—	0	5	10	20 grms. used.
Ammonium ..	33.8	33.75	33.8	33.7 c.c.
Sodium ..	33.8	33.8	33.8	33.75 "
Potassium ..	33.8	33.8	33.8	33.7 "

—I am, &c.,

J. T.

OBITUARY.

DR. EDMUND ATKINSON.

It is with regret that we record the death, on the 4th inst., of Dr. Edmund Atkinson, who, as one of the older generation of scientific men, was well known as a chemist and physicist. He was born at Lancaster in 1831, and in his early days acted as assistant to the late Sir Edward Frankland in the laboratory of Owens College, Manchester. He was also a member of the staff of Queenwood College when that school was distinguished by the presence of a band of teachers which included Professors Tyndall, Hirst, Frankland, and Dr. Debus, the latter of whom alone survives. Afterwards Dr. Atkinson was for many years Professor of Experimental Science at the Royal Military College, Sandhurst, and at the Staff College, Camberly. After he retired he continued to live at Camberly, and, as a magistrate and in other ways, he took an active part in the management of local affairs. Dr. Atkinson was perhaps best known as the translator of Ganot's "Physics." He was buried at Woking Cemetery on the 8th inst.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 16, April 17, 1900.

Heat of Combustion of Very Volatile Liquids.—MM. Berthelot and Delépine.—The combustion of organic substances can be effected with ease and precision in the calorimetric bomb by means of oxygen compressed to 25 atmospheres. Very volatile bodies, however, need special precautions to avoid partial vaporisation in the bomb, when

oxidation commences, and false calorimetric numbers result. The authors overcame these difficulties. A small glass bulb is weighed and then filled as completely as possible with the volatile liquid. After sealing this is again weighed and placed in the bomb by the side of a small weighed piece of camphor and a little gun-cotton (about 0.02 gr.) in contact with a platinum wire. After closing the bomb and admitting the compressed oxygen the gun-cotton is fired by the wire and causes the little glass bulb to explode and the combustion of the products at the same moment. By this means the heats of combustion of the ethyl aldehyde, methylal, methyl formate, ethyl formate, propyl aldehyde, and isopropyl aldehyde were determined.

New Microchemical Reaction of Palladium.—M. E. Pozzi-Escot and H. C. Conquet.—If a solution of palladium chloride and potassium nitrite are mixed and immediately afterwards excess of a caustic alkali is added (potash, soda, or ammonia), beautiful rhombohedral crystals are formed of a yellow colour, due to the formation of a double nitrite of palladium and potassium. All elevation of temperature must be avoided, since this causes a decomposition of the molecule. To obtain good crystals evaporation must be very slow.

MEETINGS FOR THE WEEK.

- MONDAY, 21st.—Society of Arts, 8. (Cantor Lectures). "The Incandescent Gas Mantle and its Use," by Prof. Vivian B. Lewes.
- TUESDAY, 22nd.—Royal Institution, 3. "Brain-Tissue considered as the Apparatus of Thought," by Alex. Hill, M.A., M.D.
- Society of Arts, 8. "The Practice of Lettering," by Edward F. Strange.
- WEDNESDAY, 23rd.—Society of Arts, 8. "Salmon Legislation," by J. Willis-Bund.
- THURSDAY, 24th.—Royal Institution, 3. "Chaucer," by the Rev. Canon Ainger, M.A., LL.D.
- Society of Arts, 4.30. "English Criminal Procedure and the Indian Code of Criminal Procedure—a Comparison," by Sir John Scott, K.C.M.G., D.C.L.
- FRIDAY, 25th.—Royal Institution, 9. "The Great Alpine Tunnels," by Francis Fox, J.P., M.Inst.C.E.
- Physical, 5. Experiments Illustrating the Aberration called Coma, by Prof. S. P. Thompson, F.R.S. "Notes on the Measurement of some Standard Resistances," by R. T. Glazebrook, F.R.S. "On the Strength of Ductile Materials under Combined Stresses," by J. J. Guest.
- SATURDAY, 26th.—Royal Institution, 3. "The Growth of Chamber Music" (with Musical Illustrations), by Sir Frederick Bridge, Mus. Doc.

Chemist, with nine years' experience in Laboratories of Iron and Steel Works, requires Situation in similar works. Abroad preferred.—Address, A. B., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Chemist (B.Sc., Ph.D.) wishes to enter Works to acquire experience. Work with organic materials preferred.—Address, H. A., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Chemist and Metallurgist, Doctor of Science (Berlin), age 30, with large experience in Chemical and Metallurgical Works, desires appointment. Speciality, Electro-chemistry. Highest references. View to partnership.—Address, W. A., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, a practical Chemist, well acquainted with the manufacture of Oil Varnishes and Lithographic Inks.—Address, M. Lévy, Printer, 9, Passage de l'Ancr, Paris.

Wanted, a superior Process for producing VENETIAN RED FROM SULPHATE OF IRON (GREEN VITRIOL). Only such persons need apply who are able to supply samples and give exact figures about consumption of fuel in the furnace, as economy in coal is the principal point.—Address, Henrik Weit, Warsaw (Poland).

LEVIGATING PAN, with one pair 4 ft. 6 in. Edge Stones, Columns, Girders, Wrought-Iron Pan, and Gearing complete. Equal to new.—Address, "Machinery," care of Lee & Nightingale, Liverpool.

THE CHEMICAL NEWS.

Vol. LXXXI., No. 2113.

ON CERTAIN PROPERTIES OF THE ALLOYS OF GOLD AND COPPER.*

By Professor Sir W. C. ROBERTS-AUSTEN, K.C.B., F.R.S.,
and
T. KIRKE ROSE, D.Sc.

THE alloys of gold and copper, which are of great industrial importance owing to their use in coinage, have not been subjected hitherto to systematic examination. It has been assumed that they differ widely from the silver-copper series, which has been studied from different points of view, but there is very little evidence on which this view can be based.

Examination with the aid of a thermo-couple and autographic recorder shows that the freezing-point curve of the gold-copper series consists of two branches setting out from the points of solidification of the pure metals and meeting at a point, which is the freezing-point of the eutectic. The eutectic contains about 82 per cent of gold, and 18 per cent of copper, or about 60 atoms of gold to 40 of copper, and solidifies at 905°. The general shape of the curve therefore resembles that of the silver-copper series when the abscissæ give the relative number of atoms.

Under the microscope, alloys containing more than 82 per cent of gold show a minutely granular structure in which it is not certain that two constituents can be distinguished. The section of standard gold containing 91.6 per cent of gold bears a close resemblance to that of standard silver prepared in the same way. The alloy with 80 per cent of gold shows the characteristically-banded eutectic structure almost exclusively, and the alloys with less gold consist of crystals of copper set in a matrix of the eutectic.

Another point of similarity between the gold-copper and silver-copper series is that both the eutectics are brittle, and show scarcely any extensibility; they differ in these respects from most other eutectics. Analysis of various portions of ingots of standard gold reveals the fact that liquation takes place as definitely as in standard silver, the difference in composition between the centre and the outside of similar ingots being, however, three or four times greater in standard silver than in standard gold. In the latter case, the centre contains from 0.3 to 1.0 part per 1000 less gold than the outside.

It follows from these results that the gold-copper series of alloys presents many points of similarity with the silver-copper series, and that the main difference is only one of degree, copper being apparently more soluble in gold in the solid state than in silver.

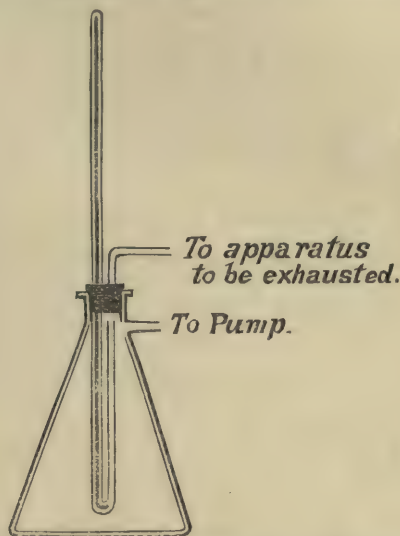
A SIMPLE AND PORTABLE GAUGE FOR VACUUM PUMP.

By E. G. BRYANT.

I HAVE found this contrivance, which is almost sufficiently described by the sketch, of considerable use, especially in lecture experiments. Its chief advantages are its portability and the difficulty of upsetting it.

The gauge is simply a U-tube with the open end long enough to reach nearly to the bottom of the safety-flask or bottle attached to the pump itself. The longer end

passes through one of the holes in the cork, and is closed at the top. The length of this limb depends, of course, on the depth of the flask. With a 16-oz. flask the two limbs can be about 7 and 15 to 17 inches respectively. Enough mercury is introduced into the tube to fill the longer end and cover the bend, or the whole tube may be filled, and the excess will run out in use and collect in the flask itself. The open end is kept close up against the cork to prevent water being splashed into it. By arranging that the bend shall be about an inch from the bottom of the flask, the gauge may be pushed down whenever the



mercury becomes hidden by the cork. The tube should be fairly strong, to resist the sudden jerk of the mercury when the pressure is relieved.

In order to obtain a gauge of the full barometric height, it would be necessary to have the short limb about $2\frac{1}{2}$ times the diameter of the long one. Messrs. P. Harris and Co., Lim., of Birmingham, have arranged to supply such a tube; the longer limb about 1 m.m. internal diameter, and both limbs graduated similarly to a syphon barometer.

Pontefract, May 12, 1900.

THE ESTIMATION OF BENZOL IN COAL-GAS.

By O. PFEIFFER.

THE volumetric analysis of gases does not allow of the separation of the gaseous hydrocarbides from the fumes of the heavy hydrocarbides which, grouped under the name of ethylene and benzol, are the most important with regard to illuminating gas. Among the numerous methods which have been proposed, that of Harbeck and Lunge is the most to be trusted (*Zeit. Anorg. Chemie*, 1898, xvi., 41). It is based on the separation of the benzol as a binitrated product; the following is the method of procedure:—With the aid of an aspirator fitted with a thermometer and a manometer about 10 litres of the gas are passed through the nitrating mixture. The acid gases are absorbed by tubes filled with caustic potash or soda. The nitrating mixture is poured over a layer of ice, neutralised with soda, and treated with ether. After driving off the solvent, the dinitrobenzol is dried either by heating or *in vacuo*, and weighed. But as the nitrating mixture absorbs a part of the carbonic oxide, this method does not give altogether exact results, and it becomes necessary to modify it in the following manner:—The

* Abstract of a Paper read before the Royal Society, May 10, 1900.

apparatus, for both the measurement and the nitration of the gas, consists of a separating funnel of 3 or 4 litres capacity, accurately calibrated. After having introduced the gas, the temperature and pressure are noted, and 10 c.c. of the nitrating mixture are run in; this mixture consists of equal parts of nitric acid, of 1.52 density, and concentrated sulphuric acid. When the absorption of the benzol fumes is complete, 100 c.c. of water are run into the funnel, well shaken, and transferred to a smaller separating funnel, and the acid neutralised by means of 40 grms. of crystallised soda. It is then treated two or three times over with 50 c.c. of ether, and, after having got rid of the solvent, the dinitrobenzol is dissolved in absolute ether; the liquor is then filtered through a layer of calcined soda and collected in a small crystallising jar. After having evaporated the ether the residue is dried over sulphuric acid. To transform the weight of the dinitrobenzol into per cent (by volume) of benzol vapour we use the formula—

$$\frac{36080}{J} \cdot g \frac{273 + t}{b} = \text{per cent benzol vapour};$$

in which J represents the capacity of the large separating funnel, g the weight found, t the temperature, and b the pressure. We may also estimate the benzol vapour, with very close results, in the following manner:—We must first know the specific gravity, s , of the heavy carbides of hydrogen—a constant which can be obtained from the specific gravity, S , of the gaseous mixture, and from the proportion (per cent) in CO , CH_4 , . . . &c., according to the formula—

$$s = 100S - (\text{CO} \cdot 0.9621 + \text{CH}_4 \cdot 0.5530 + \text{H} \cdot 0.0692 + \text{N} \cdot 0.9701 + \text{CO}_2 \cdot 1.5197) \frac{1}{C_n H_m}$$

By calling the total volume of the heavy hydrocarbides v , the benzol vapour contained in the gas = $\frac{(5 - 0.9674) v}{1.7367}$ per cent by volume.—*Journal für Gasbeleuchtung und Wasserversorgung*, xlii., 697.

ON THE ALKALOIDS OF AUSTRALIAN PLANTS.*

By G. HARKER, B.Sc.

BEFORE beginning this investigation it was necessary to become conversant with the known methods for the extraction of alkaloids from plants and their subsequent purification. In obtaining information respecting the alkaloids in Australian plants already investigated, I was specially indebted to Mr. Maiden, whose papers I also made use of.

The following plants were examined:—

MONIMIEÆ.—*Daphnandra micrantha* (Bentham). This plant has been examined by Dr. Bancroft physiologically and found to be active. In this investigation a considerable quantity of an alkaloid was isolated by me, and a large number of tests applied. The alkaloid, which so far as could be seen was amorphous, was present in the bark, the leaves containing a glucoside.

LAURINEÆ.—*Cryptocarya obovata* (R. Brown). No alkaloid present.

PITTOSPOREÆ.—*Pittosporum undulatum* (Andrews). No alkaloid.

EUPHORBACEÆ.—*Phyllanthus ferdinandi* J. Mueller. This plant contained a small trace of a volatile alkaloid.

In the case of each plant the bark and leaves were examined carefully. A most careful search was made for either fixed or volatile alkaloid, and large quantities of material were worked upon so that small traces should not be missed.

ESTIMATION OF ARSENIC IN METALS AND ALLOYS.

By A. HOLLARD and L. BERTIAUX.

THIS method is based on the separation of arsenic by distillation; though not entirely new it has the advantage over similar methods of being applicable in the presence of a considerable quantity of antimony, without requiring more than one distillation, and further, it is very rapid. The apparatus used is the same as that already described in the paper on the commercial analysis of copper (*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 8).

5 grms. of the granulated metal are placed in the flask with 50 grms. of ferric sulphate freed from all traces of nitrous fumes by evaporation with an excess of sulphuric acid. Then by means of the funnel 150 c.c. of pure hydrochloric acid are run in, and the tap turned off, after seeing that the oil-bath containing the U-tube is at 150—175°; the flask is then gently heated. The metal dissolves, and the arsenic distils over in the form of arsenious chloride; this chloride is collected in the test-jar, which already contains 50 c.c. of water. The operation is stopped when 35 c.c. of liquid have passed into the test-jar; this will take about half an hour from commencing to heat the flask. Under these conditions the arsenic only passes into the test-jar, the antimony remains in the U-tube which contains glass beads; this U-tube also prevents the passage of any projections which might leave the flask.

The arsenious solution is then titrated with iodine. This method, however, is not absolutely correct when applied to the estimation of arsenic in metallic antimony, as 0.0015 gm. of antimony passes over on distillation.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 8.

THE DETECTION AND ESTIMATION OF FORMIC ALDEHYDE.

By C. NEUBERG.

THE author has observed that *p*-dihydrazinodiphenyl, $\text{NH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$, unites with formic aldehyde, giving a methylenic compound—



in the form of a yellow precipitate consisting of microscopic needles. This precipitate forms rapidly in the cold, and instantaneously at 60°. It is insoluble in organic liquids of the most varying characters, in alkalis, and in alkaline carbonates. It is rapidly destroyed by mineral acids, and acetic acid. It melts towards 220°, and decomposes at 240°. To prepare this body the author recommends the gradual addition of the solution of formic aldehyde at 40 per cent to an aqueous solution, heated to 60°, of hydrochlorate of *p*-dihydrazinodiphenyl; this latter salt must be absolutely pure and colourless, otherwise there will be strongly coloured accessory products formed.

The precipitate appears even when there is only 1/5000th part of formic aldehyde in solution, but it is necessary in such a case to wait for a few minutes.

Furfural, which has some of the same reactions as formic aldehyde, does not give this one any more than do the other aldehydes and ketones. If one of these latter happens to be present, two volumes of alcohol should be added, so as to dissolve the compound it might form with the dihydrazine. The precipitate must then be treated with alcohol until the foreign matter is entirely removed.

Commercial hydrochlorate of dihydrazinodiphenyl may be used for qualitative work, but for estimation the cooled pure salt must be used, and the liquid containing the formic aldehyde added with continuous stirring; it is then gradually heated to 60° and left to stand, then filtered, washed with boiling water, alcohol, and dry ether, and

* Abstract of a Paper read at the Melbourne Meeting of the Australasian Association for the Advancement of Science, Jan., 1900.

dried at 90°. The bright yellow colour should remain. For the titration to be exact the solution ought to contain 1 to 2 per cent of formic aldehyde. The results are always approximate, but the method is of advantage when there are other aldehydes and ketones present. We might also titrate volumetrically the excess of dihydrazine after filtering the precipitate.—*Berichte*, xxxii., p. 1951.

LABORATORY METHOD FOR THE CONTINUOUS AND UNIFORM GENERATION OF ACETYLENE, AND FOR ITS PURIFICATION.*

By J. A. MATHEWS.

For most purposes in which it is desired to employ a stream of acetylene, no purification is necessary, provided the gas has been properly generated from the usual quality of commercial carbide now being produced. Analyses from various sources show that the impurities in acetylene from this source rarely amount to 1 per cent, and a good part of this is likely to be nitrogen. The combined amounts of hydrogen sulphide, hydrogen phosphide, and ammonia seldom exceed 0.2 per cent. In order that the amount of impurities may be as small as possible it is necessary that the gas be produced in the cold. This cannot be done when water is allowed to drip slowly upon the carbide, and furthermore this method causes the gas to be given off spasmodically, and the lime residue often bubbles or froths to such an extent that solid matter in considerable amounts may be carried over with the gas. In obviating all these difficulties the following method has proved successful:—

The fragments of calcium carbide are placed in a wide-mouthed bottle. They may, with advantage, be suspended in a basket of coarse wire netting, which will keep the carbide away from the lime residue, and also allow it to be withdrawn at any time. The carbide is covered with an abundance of absolute or 95 per cent alcohol, and the bottle closed with a two-hole stopper. Through one hole water can be led from a reservoir bottle, and in the other an outflow tube is fitted. If 95 per cent alcohol is used, the water therein serves to start the generation of acetylene and to expel the air from the apparatus. If, now, water be added drop by drop, it comes slowly into contact with the carbide, and a steady production of acetylene results. Unless the amount of alcohol present is very small and the rate of generation very rapid, no material rise in temperature ensues. After the addition of water has been stopped, the evolution of gas may be allowed to proceed until the bubbling ceases; the alcohol may then be decanted from the residue and distilled, and, rejecting the first few cubic centimetres, the rest of the distillate will be nearly absolute alcohol.

If it is desired to purify the acetylene, any one or more of several methods may be employed. No single purifying agent which has as yet been advocated meets all the requirements. For general convenience and thoroughness the following combination of methods is suggested:—

The acetylene generated as described above is passed into a solution of 15.6 parts of crystallised copper sulphate in 100 parts of water, to which is added 5 parts of dilute sulphuric acid (Hempel and Kahl, *Zeit. Angew. Chemie*, liii., 1898), 1 volume of sulphuric acid to 4 volumes of water. This solution, besides retaining any vapour of alcohol and also the ammonia and hydrogen sulphide, is especially useful for absorbing hydrogen phosphide. As an additional safeguard the acetylene is next passed through one or two towers filled with coarse

bits of pumice stone which have been saturated with an acetic or sulphuric acid solution of chromic acid (Ullmann, *Z. für Gasbeleucht.*, 1899, xlii., 198, 374), or, in place of a second tower, a strong sulphuric acid solution of chromic acid may be used. By this means any of the three chief impurities, which might escape absorption in the copper sulphate solution, will be completely oxidised. A small amount of these purifying materials will serve for a large volume of gas, and the acetylene should issue both dry and pure and possessing a faint and agreeable odour. A return of the strong irritating odour indicates that the purifiers have become exhausted.

The purification of acetylene by means of moist chloride of lime or sodium hypochlorite, as suggested by Odernheimer (*Chem. Zeit.*, xxii., 21) and Lunge (*Zeit. Angew. Chem.*, 1897, p. 651) or as modified by Wolff* (*Chem. Zeit.*, xxii., 281), is impracticable because of the instability of the solutions and because chlorine and chlorination products of acetylene are produced, which must then be removed by lime. Frank's method (*Zeit. Angew. Chem.*, 1898, p. 1050), using strongly acid solutions of copper or iron chloride, does not seem very efficient, nor is the employment of bromine as a purifier convenient for laboratory use. The combination of Hempel's and Ullmann's methods seems to meet all the requirements and is easily and conveniently arranged.

THE CARBIDE OF GOLD.†

By J. A. MATHEWS and L. L. WATERS.

EXPLOSIVE compounds resulting from the action of acetylene or coal-gas upon alkaline solutions of cuprous, argentous, and mercuric salts have been known for many years. These compounds are for the most part flocculent precipitates which retain water with more or less tenacity, and at temperatures which will render them anhydrous they are apt to explode violently. The earlier investigators of these acetylides did not recognise them as true carbides, and their analyses show the presence of hydrogen and oxygen, which are reported as constituent atoms of the molecule. Berthelot (*Ann. Chim. Phys.* [4], ix., 425), who did a great deal of work upon acetylene derivatives, speaks of copper acetylide as "cupro-acetyloxide," and gives it the formula $(C_2Cu_2H)_2O$. Reboul (*Comptes Rend.*, liv., 1229) gives silver acetylide as $(C_2HAg)_2 + Ag_2O$, and Blochmann (*Ann. Chem.*, Liebig, clxxiii., 176, 177) gives respectively $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$. All of these might better be written C_2Cu_2 or C_2Ag_2 plus more or less water. Miasnikoff (*Ann. Chem.*, Liebig, cxviii., 330) gives silver acetylide as $C_2H_2Ag_2$. Keiser (*Ann. Chem. Z.*, xiv., 285) showed, however, that when properly dried these two acetylides are simply C_2Ag_2 and C_2Cu_2 , and later (*Ibid.*, xv., 535) produced mercuric acetylide, HgC_2 , which is also hydrated at the time of its formation.

Berthelot (*Ann. Chim. Phys.* [4], ix., 425) seems to be authority for the statement which appears in a number of old chemical works, but for which these do not give him credit, that by passing acetylene through aurous thio-sulphate, a yellow explosive precipitate is formed. He gives no analysis of the product, and does not give any suggestions as to its probable constitution.

We have recently investigated this interesting compound, which proves to be analogous to the copper and silver compounds, its formula being aurous carbide, Au_2C_2 .

* Contributions from the Havemeyer Laboratories, Columbia University, No. 16. *Journal of the American Chemical Society*, vol. xxii., No. 2.

* Wolff treats the gas first to remove ammonia and then with hypochlorite, thus eliminating the danger of forming nitrogen chloride, which he says is possible.

† Contributions from the Havemeyer Laboratories, Columbia University, No. 17. Reprinted from the *Journal of the American Chemical Society*, vol. xxii., No. 2.

In the preparation of aurous sodium thiosulphate we followed the method of Fordos and Gélis (*Ibid.* [3], xiii., 394, 1845). Pure auric chloride was dissolved in 50 parts of water; 3.2 parts of sodium thiosulphate were dissolved in the same amount of water. The solution of gold was added to the thiosulphate very slowly and with constant stirring. A slight odour of sulphur dioxide was noticed, and a little sulphur separated.

The solution was filtered, and the sodium aurous thiosulphate was precipitated with absolute alcohol. It was not re-crystallised. The principal reaction is said to be $8\text{Na}_2\text{S}_2\text{O}_3 + 2\text{AuCl}_3 = 2\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 + 2\text{Na}_2\text{S}_4\text{O}_6 + 6\text{NaCl}$.

This compound forms a colourless precipitate, very soluble in water but insoluble in alcohol. To form aurous carbide an aqueous solution of the sodium aurous thiosulphate is made strongly alkaline with ammonia and a slow stream of acetylene passed through. The solution remains colourless for a short time and then becomes yellow, and finally a yellow flocculent precipitate appears. In this respect it differs from silver and copper carbides, which form almost instantly, and hence are used to test for the presence of minute quantities of acetylene. The precipitate is filtered off, washed with water and alcohol, and dried in a desiccator over sulphuric acid.

Properties.—When thoroughly dried, the carbide of gold is highly explosive either upon rapid heating, by a blow, or even by brushing with a camel's hair brush. The explosion generates sufficient heat to produce flame, and the gold is left in an extremely finely divided condition and black. Carbide of gold is easily decomposed by hydrochloric acid, giving acetylene and leaving a black residue of aurous chloride. The presence of acetylene was shown by passing it into ammoniacal silver nitrate, in which it produced silver acetylide. The aurous chloride was tested by boiling, which gave auric chloride and metallic gold. By boiling gold carbide with water it is decomposed into its constituents, no acetylene being produced. Cupric sulphate and neutral ferric chloride do not decompose it in the cold; when anhydrous it becomes darker in colour and of a brown tint, and if heated very gradually decomposes without explosion. This fact was made use of in the determination of gold. The sample to be analysed was heated in the air-bath very slowly until a temperature of 180° to 200° was indicated, and then ignited in the flame of a Bunsen burner. The black mass becomes yellow by the burning off of the carbon and annealing of the gold. The analyses resulted as follows:—

	Weight of sample.	Gold found.	Gold per cent.	Theory for Au_2C_3 .
I.	0.029	0.0273	94.14	94.25
II.	0.0174	0.0164	94.25	94.25

One sample of aurous carbide after two days in the desiccator lost no weight at 100°C ., nor was loss experienced on renewed heating up to 120°C . Another sample that had not stood so long over sulphuric acid lost 0.0004 gm. at 100° . By rapid heating in the air-bath explosions were obtained at various temperatures from 83° to 157°C . No attempt was made to secure especially uniform heat at all parts of the air-bath, but the thermometer bulb was in all cases very close to the dish containing the explosive compound. It seems then that the rate of heating has most to do with effecting the decomposition of gold acetylide. The violence of the explosion was shown by several unexpected explosions. In one case about 15 or 20 m.grms. of the substance were on a watch-glass. In trying to remove a small fragment with the point of a knife, the whole mass exploded with a sharp report, and the watch-glass was broken into a score of pieces. In another instance, while brushing some of the carbide from a filter-paper with a camel's hair brush into a dish, the particles adhering to the paper exploded with a loud report and flame, and the filter-paper was badly torn, but the bulk of the material, which was not over an inch or two away, was not exploded by the con-

cussion. The same fact was noted in the first explosion above, in which case the watch-glass was standing beside a crucible containing quite a large amount of dry gold carbide.

No other aurous solutions were tested with a view to obtaining gold carbide. From auric chloride in aqueous solution metallic gold is precipitated by acetylene.

A solution of auric chloride made alkaline with potassium hydroxide does not give a precipitate under similar conditions, nor does an aqueous or ammoniacal solution of potassium auric cyanide give a precipitate when acetylene is passed into it.

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.*

By LILY G. KOLLOCK.

(Continued from p. 233).

GOLD SEPARATIONS.

SMITH and Muhr (*Am. Chem. Journ.*, xiii., 417) report the separation of gold from palladium, platinum, zinc, cobalt, nickel, and copper.

Gold from Palladium.—It has been previously shown that palladium is not deposited with a current of 0.01 A in the presence of an excess of potassium cyanide. With a current liberating eight-tenths c.c. of oxyhydrogen gas a minute, and the solution containing $1\frac{1}{2}$ grms. of potassium cyanide, 0.1162 gm. of gold was deposited in from twelve to fourteen hours.

In accordance with this suggestion, the following conditions were obtained:—Two grms. of potassium cyanide were added to a solution of gold chloride containing 0.1256 gm. of metal and palladium chloride equivalent to one-tenth gm. of metallic palladium. This was diluted to 250 c.c. The current used was N.D.₁₇₅ = 0.06–0.09 A and $V=1.5$. The temperature during the decomposition was 65° . In five hours the current was raised to 0.09 A. The gold was found to be completely deposited and free from palladium (see Table XVII.).

Gold from Copper.—In the report referred to, the separation of gold from copper in cyanide solution took place with a current liberating eight-tenths c.c. of oxyhydrogen gas at the ordinary temperature in about twelve hours.

It was found that by heating the solution to 65° the precipitation was more rapid, but required more cyanide in order to keep the copper from being deposited with the gold. To a solution of gold chloride containing 0.1665 gm. of metallic gold and copper sulphate containing one-tenth gm. of copper were added 4 grms. of potassium cyanide. The solution (250 c.c.), warmed to 65° , was electrolysed with a current of N.D.₁₇₅ = 0.05–0.07 A and $V=1.7$ for two and one-half hours. In this time 0.1667 gm. of gold was obtained. There was no reaction for copper when the deposit treated with nitric acid was tested for that metal (see Table XVIII.).

Gold from Nickel.—The conditions under which this separation is made are similar to those obtained under the separations of silver and mercury from nickel. The solution of gold chloride used was equivalent to 0.1610 gm. of metallic gold, and nickel nitrate contained one-tenth gm. of nickel. They were converted into their double cyanides by the addition of 4 grms. of potassium cyanide. A current of N.D.₁₀₀ = 0.05 A and $V=1.5$ was passed through the solution (125 c.c.) at 60° for six hours. The gold on examination contained no nickel (see Table XIX.).

Gold from Cobalt.—More difficulty was experienced with the separation of these metals than with the pre-

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xxi., No. 10.

TABLE XVII.

Gold. Grm.	Palladium. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Gold found. Grm.
0'1256	0'1	2	125	N.D. ₁₀₀ =0'06—0'03 A.	2'5	65°	6	0'1250
0'1256	0'1	2	250	N.D. ₁₇₅ =0'06—0'09 A.	2'5	65°	6	0'1257

TABLE XVIII.

Gold. Grm.	Copper. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Gold found. Grm.
0'1665	1	2	250	N.D. ₁₇₅ =0'07 A.	1'7	65°	2½	0'1667
0'1627	1	2	250	" =0'05—0'08 A.	1'9	65°	3	0'1627

TABLE XIX.

Gold. Grm.	Nickel. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Tempera- ture.	Time. Hours.	Gold found. Grm.
0'1567	0'1	4	125	N.D. ₁₀₀ =0'05 A.	1'7	65°	7	0'1567
0'1610	0'1	4	125	" =0'05 A.	1'5	60°	7	0'1603

TABLE XX.

Gold. Grm.	Cobalt. Grm.	Cyanide. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Dilution. C.c.	Time. Hours.	Gold found. Grm.
0'1610	0'1	4	125	N.D. ₁₀₀ =0'05—0'08 A.	1'7	60°	125	6½	0'1612
0'1610	0'1	4	125	" =0'05—0'08 A.	1'7	60°	125	6	0'1608
0'1495	0'1	4	250	N.D. ₁₇₅ =0'05—0'08 A.	1'7—2	60°	250	6	0'1497

TABLE XXI.

Gold. Grm.	Zinc. Grm.	Cyanide. Grms.	Current.	Voltage.	Dilution. C.c.	Temperature.	Time. Hours.	Gold found. Grm.
0'1495	0'1	4	N.D. ₁₀₀ =0'06 A.	2'66	125	60°	7	0'1490
0'1608	1	4	N.D. ₁₇₅ =0'06 A.	2'7	250	65°	7	0'1602

TABLE XXII.

Mercury. Grm.	Sodium sulphide (sp. gr. 1'19). C.c.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Mercury found. Grm.	Error. Grm.
0'1403	25	100	N.D. ₁₀₀ =0'11 A.	2'5	70°	5	0'1400	0'0003
0'1403	25	100	" =0'12 A.	2'7	70°	5	0'1404	0'0001

TABLE XXIII.

Copper. Grm.	Nitric acid. C.c.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Copper found. Grm.
0'1398	10	100	N.D. ₁₀₀ =0'03 A.	1'7	Cold	16	0'1396
0'1398	10	100	" =0'09 A.	1'9	70°	16	0'1397
0'1398	10	100	" =0'09	1'9	65°	16	0'1398

ceding. Four grms. of potassium cyanide were added to the solution of gold chloride and cobalt nitrate equivalent to one-tenth grm. of cobalt. The current used for the deposition of the gold was N.D.₁₀₀=0'05 A and V=1'7. The electrolysis was carried out at 60° C. It was found advantageous before the end to add 1 c.c. of a 20 per cent sodium hydroxide solution, and raise the current to 0'08 A, in order to deposit the last trace of gold. In this way the gold was entirely deposited in seven hours free from cobalt (see Table XX.).

Gold from Zinc.—These metals were successfully separated according to the following conditions:—Four grms. of potassium cyanide were added to a solution of gold chloride and zinc sulphate containing one-tenth grm. of zinc. The current acting upon the double cyanide was N.D.₁₀₀=0'06 A and V=2'66. The temperature of the solution was 60°. In seven hours the deposition was complete. No zinc was found with the gold (see Table XXI.).

Gold from Platinum.—To the solution of gold chloride containing 0'1576 grm. of gold and platinic chloride equivalent to 0'125 grm. of platinum, were added 1½ grms. of potassium cyanide. The volume of the solution was 250 c.c. A current of N.D.₁₇₅=0'01 A and V=2'7 was used. The temperature was 70° C. In three hours the gold was entirely precipitated. No platinum was deposited with the gold. The deposit weighed 0'1479 grm.

Mercury from an Alkaline Sulphide Solution.—In 1891 Smith made the statement that mercury obtained as mercuric sulphide during analysis may be accurately estimated electrolytically. The sulphide was dissolved in sodium sulphide of sp. gr. 1'19, and electrolysed with a current generating 1 c.c. of oxyhydrogen gas per minute acting during the night. The mercury was always compact and grey in colour.

In working out conditions for the determination of mercury by this method, 25 c.c. of sodium sulphide were added

to a solution of mercuric chloride containing 0.1403 grm. of mercury. This solution, diluted to 125 c.c., was electrolysed at 70° C. by a current of N.D.₁₀₀=0.11 A and V=2.5. In five hours the mercury was entirely deposited; it was light grey in colour. Slightly warm water was used in washing the deposit (see Table XXII.).

COPPER.

"Moore advises dissolving the recently precipitated copper sulphide obtained during the ordinary course of analysis in potassium cyanide, and after the addition of an excess of ammonium carbonate, electrolyse the warm (70°) solution" (Smith's "Electro-chemical Analysis," p. 61). According to this suggestion, the following conditions for the determination of copper were found to give good results:—The copper sulphate solution used contained 0.1270 grm. of metallic copper; this was precipitated as sulphide, which was dissolved in 2 grms. of potassium cyanide and ammonium carbonate added. The solution, diluted to 125 c.c., was heated to 70° C. and electrolysed with a current of N.D.₁₀₀=0.02–0.07 A and V=4. In three hours the copper was completely deposited. The copper was found to weigh 0.1269 grm.; that is, 0.0001 grm. less than the theoretical amount.

Copper from Nitric Acid Solution.—Copper has also been successfully determined electrolytically in a nitric acid solution (*Am. Chem. Journ.*, xii., 329). A solution containing 10 c.c. of concentrated nitric acid was diluted to 100 c.c. and electrolysed. The current used was N.D.₁₀₀=0.03 A and V=1.7. At the ordinary temperature in sixteen hours 0.1396 grm. of copper was precipitated. The solution, treated with ammonium hydroxide, showed that the copper had been entirely deposited. With a temperature of 65° and a current of N.D.₁₀₀=0.09 A and V=1.9 in five hours 0.1397 grm. of copper was found, and another determination under identical conditions gave the theoretical amount of copper present (see Table XXIII.).

Cadmium from Sulphuric Acid Solution.—Smith (*Am. Chem. Journ.*, ii., 42) describes the quantitative deposition of cadmium from its sulphuric acid solution. Cadmium oxide was dissolved in sulphuric acid. The solution contained 2 c.c. of free sulphuric acid of sp. gr. 1.095.

The volume of the solution was 25 c.c. In two hours the cadmium was completely precipitated. The amount of cadmium present was 0.0931 grm. The following conditions were found to give good results by this method:—A solution of cadmium sulphate containing 0.1599 grm. of metal, after adding 3 c.c. of sulphuric acid (sp. gr. 1.09) and diluting to 125 c.c., was electrolysed with a current of N.D.₁₀₀=0.078 A and V=2.61. The temperature during the electrolysis was 65°. In five hours the deposition of cadmium was complete. The metal weighed 0.1604 grm.

(To be continued.)

A "Thrift Chat."—A large number of the workpeople employed by the United Alkali Company, Ltd., attended a "Thrift Chat," which took place at St. Rollox Chemical Works, Glasgow, a few days ago. Mr. James McCulloch presided, and a representative of the Glasgow Thrift Society gave an address, at the conclusion of which there was a distribution of thrift literature. The Thrift Chat owes its existence to the National Thrift Society, which some years ago hit upon the plan of holding friendly talks with the workpeople employed in factories, mills, foundries, shipbuilding yards, and so on, not in outside places of meeting, but in the works themselves. The talk usually takes place at the end of the mid-day meal hour. The plan is excellent, and the "Chats" are growing in popularity, not only amongst the workers but amongst the employers, who are giving the Society every facility for the dissemination of its helpful doctrines.

ON THE PROGRESS OF CHEMISTRY IN GREAT BRITAIN AND IRELAND DURING THE NINETEENTH CENTURY.*

PART I.—FROM THE BEGINNING OF THE CENTURY TO THE
FOUNDATION OF THE CHEMICAL SOCIETY (1841).

By T. E. THORPE, LL.D., F.R.S.,
President of the Chemical Society.

(Continued from p. 235).

THE third decade of the century saw the rise of Faraday, Graham, and Edward Turner. Faraday had thrown up book-binding in 1813, and attached himself to the Royal Institution, getting his "baptism of fire" in working upon Dulong's newly-discovered nitrogen chloride, which was then occupying Davy's attention. He assisted Davy, too, in his work on iodine, on the torpedo, on the nature of the diamond, on euchlorine, and on the chlorides of phosphorus, and in his memoir on "Some Combinations of Phosphorus" the master pays a well-merited tribute to the "accuracy and steadiness of manipulation of his assistant."

Although Davy had propounded his proofs of the elementary nature of chlorine as far back as 1810, and although these had been strengthened by his work on iodine in 1814, his doctrine was not universally accepted, the Scotch teachers in particular, notably Murray and Ure, even as late as 1818, making repeated and determined attempts to subvert it. Faraday did yeoman service in repelling the attack, which eventually degenerated into a wordy warfare between Murray and John Davy.

With the beginning of 1820 Faraday may be said to have served his apprenticeship to science. He had already contributed some two score notices and papers to the *Quarterly Journal of Science*, and had published his remarkable work with Stodart, a surgical instrument maker, on wootz and other alloys of steel. He had discovered tetrachlorethylene, perchlorethane, and ethylene diiodide, an account of which constitutes his first paper in the *Philosophical Transactions*, and shortly afterwards he described, with Richard Phillips, a new compound of chlorine and carbon, first observed by Jölin, of Abo, and now known as hexachlorobenzene. In 1823 appeared his memorable paper "On Fluid Chlorine," and immediately afterwards were liquefied hydrogen chloride, sulphur dioxide, carbon dioxide, sulphuretted hydrogen, euchlorine, and nitrous oxide. It should be stated, however, that Monge and Clouet had already condensed sulphur dioxide, probably before the year 1800, and that Northmore, with the assistance of Accum, had obtained liquid chlorine in 1806 by compression at ordinary temperatures (*Nicholson's Journal*, 12 and 13). Northmore's description of the properties of liquid chlorine is so explicit that it is remarkable that the significance of his observation should have escaped notice. The name and fame of the Royal Institution are indissolubly connected with the work so auspiciously begun by Faraday, and with the liquefaction and solidification of air and hydrogen by my predecessor in this chair this chapter in the history of physical science closes with the closing years of the century. It will ever be accounted among the triumphs of the 19th century that it has effected the removal of those artificial boundaries—the hard and fast lines of demarcation—implied by terms which have now no other rational meaning than as denoting states of physical aggregation. Nor will it be forgotten that it is largely to the labours of our countrymen, Dalton, Faraday, Andrews, and Dewar, that this achievement is to be ascribed.

In 1825 Faraday discovered benzene. He found it among the products furnished by the operations of the Portable Gas Company. Although he ascertained that the density of its vapour was 39, hydrogen being 1, the

* Presidential Address to the Chemical Society, 1900.

significance of that circumstance was not perceived at the time. The work of Ampère and Gay Lussac, in fact, was not really understood or appreciated at this period, and the conception of Avogadro lay dormant. "With regard to the composition of this substance," wrote Faraday, "my experiments tend to prove it a binary compound of carbon and hydrogen, two proportionals of the former element being united to one of the latter." What Faraday's bicarburet of hydrogen has developed into need not now be told. The work which has accumulated round this single substance during the seventy-five years which have elapsed since it has been known constitutes one of the most astonishing records of intellectual and industrial activity of which history has any record.

Faraday's next contribution to aromatic chemistry consisted in a study of the action of sulphuric acid on naphthalene, or "naphthaline" as it was then termed—a name which we owe to Dr. John Kidd, who lectured on chemistry at Oxford in the early part of the century, and who accurately described the main properties of the hydrocarbon, which appears to have been first observed in 1819 by Alexander Garden, of Old Compton Street, Soho, where the London Chemical Society had its habitation. The products obtained by Faraday are now known as α - and β -naphthalenesulphonic acids, the salts of which he described. It is noteworthy that in this year (1826) the Friday evening discourses at the Royal Institution were instituted by Faraday, with a view, as he says, to facilitate our object of attracting the world and making ourselves, with science, "attractive to it," and that this work on naphthalenesulphonic acid was the subject of the first chemical discourse of the series. Unpromising as it might seem, we may be quite sure that Faraday made it attractive.

Although Faraday continued to occupy himself at times with chemical subjects, even to the end of his tenure of the Fullerian professorship at the Royal Institution, he gradually became more and more absorbed in those memorable physical researches with which his name will ever be associated. The more important portion of his chemical work was practically all done before the end of 1826, and, curiously enough, one of the last inquiries with which he concerned himself in that year serves to connect him with Graham, whose services to science began in that year. It happened that Faraday, in 1823, had made some observations, perhaps among the earliest ever made, which served to establish what we now know as the transpiration of gases, but their accuracy had been doubted by Davy, who, three years later, repeated them. Davy's experiments on this subject constitute, in fact, the last ever performed by him in the laboratory of the Royal Institution. Faraday independently repeated the observations of 1823, and established their validity.

Graham's chief work, of course, lay in the borderland between physics and chemistry. The finite extent of the atmosphere; the absorption of vapours by liquids; the law of the diffusion of gases; the motion of gases; the diffusion of liquids; osmotic force; on liquid transpiration; on molecular mobility of gases; the absorption and dialytic separation of gases by colloid septa; on occlusion of gases; hydrogenium—however different may be the titles of his papers, all his work centred round conceptions of atoms and molecules and their motions. Of his contributions to pure chemistry, the most important was that "On the Arseniates, Phosphates, and Modifications of Phosphoric Acid"—the first of his papers sent to the Royal Society, to which it was communicated by Edward Turner, whom he succeeded a few years later in the Chair of Chemistry at University College. This memoir established the existence of three modifications of phosphoric acid—ortho-, pyro-, and meta-phosphoric acid. The first, or ordinary phosphoric acid, has been known for at least three centuries; pyrophosphoric acid was discovered by Clark, whom Graham succeeded as Lecturer on Chemistry at the Mechanics' Institute, Glasgow; metaphosphoric acid was now made known for the first

time. The paper is memorable from the circumstance that it first definitely indicated the idea of *basicity*.

Graham's memoirs on the part played by water as a constituent of salts, and on the constitution of salts, are logically connected with and dependent on this paper. Indeed, nothing is more remarkable in Graham's work than the continuity of idea which pervades it. Just as the long succession of memoirs on the molecular movements of gases and liquids gave a definiteness and precision to the conception of the intestinal motions in matter, so his work on acids and salts served to establish the constitutional analogy between these substances.

Edward Turner was born in Jamaica in 1798, and, after studying medicine at Edinburgh, passed over to Göttingen, where he worked under Stromeyer. In 1824 he became a lecturer in Edinburgh, and here published an "Introduction to the Study and Laws of Chemical Combination," which he subsequently worked into his excellent "Elements of Chemistry," one of the standard text-books of the time, and by which he is mainly remembered. In 1828 he was made Professor of Chemistry in the newly-created University of London, now known as University College, and died in 1837 in the fortieth year of his age. Among his pupils was the late Sir Richard Quain, who described him as a lucid lecturer and a good analyst. Turner was indeed an excellent manipulator, and his analytical and determinative work was of a high order. He is especially to be remembered for his determinations of the atomic weights of lead, chlorine, silver, barium, mercury, nitrogen, and sulphur; they were the first atomic weights to be accurately ascertained by a British chemist, and are worthy to be ranked with the determinations of Berzelius. Turner's numbers were not only valuable as constants, but they were of theoretical importance as directly impugning the validity of Prout's hypothesis, which, mainly on the authority of Thomas Thomson, who had sought to support it by what is perhaps the weakest experimental evidence ever put forward, was part of the current doctrine of the time in this country. On Thomson's work Berzelius had passed what is probably the most scathing criticism he ever uttered:—"This work belongs to those few productions from which science will derive no advantage whatever. Much of the experimental part, even of the fundamental experiments, appears to have been made at the writing-desk; and the greatest civility which his contemporaries can show its author is to forget that it was ever published" (*Fahresber.*, 1827, 77).

Turner pointed out (1) that the atomic weights hitherto commonly used by British chemists had been adopted without due inquiry, and that several of the most important ones were erroneous, and (2) that the hypothesis that all equivalents are multiples of a whole number of the equivalent of hydrogen was inconsistent with the state of chemical knowledge at the time, being at variance with experiment. "Under such circumstances Dr. Prout's hypothesis, as advocated by Dr. Thomson—that all atomic weights are simple multiples of that of hydrogen—can no longer be maintained. I grant most willingly that a system of whole numbers, considered as moderate approximations, may, with advantage, be retained for the use of medical men, students, and manufacturers; but as the strict representative of scientific truth, applicable to all the purposes of science, this hypothesis is at present untenable. Let me not, however, be misunderstood: I mean simply to affirm that the experiments by which it has been attempted to prove the truth of this hypothesis are inaccurate; I may go further, and declare it to be not only unsupported by evidence, but to be at variance with the most exact analytic researches which have been conducted. I deny not that some simple relation subsists among atomic weights, and that their ratios may possibly be expressed by some series of numbers; but at present no one has assigned any physical cause for the existence of such a relation; no such relation has hitherto been discovered; nor, as appears to me, has analytical che-

mistry attained that degree of perfection which can justify anyone in finally asserting or denying its existence." The position thus taken up by Turner is precisely that to which Stas arrived half a century later, after an inquiry which will ever remain a model of analytical skill.

William Hyde Wollaston died on December 22nd, 1828, at the age of sixty-two; Thomas Young on May 10th, 1829, aged fifty-six; and Humphry Davy on May 29th, 1829, aged fifty-one. The passing away of three such men in the ripeness of their intellectual vigour, and in such quick succession, profoundly affected the whole scientific world. They had been colleagues during life, each holding high office in the Councils of the Royal Society, and were, with Dalton, the brightest ornaments of one of the most glorious epochs in the history of physical science in this country. At present we are only concerned with Wollaston and Davy. On Davy's triumphs, on his mental powers, and on the characteristics of his genius, it is unnecessary now to dwell; with the exception of that of Dalton, there is probably no personality in the history of British chemistry with which we are more familiar. Wollaston is less well known; his achievements, indeed, were less calculated to strike the popular imagination than those of his great contemporaries. But this silent, austere man, who lived in and for his laboratory and his library, his only relaxation being an occasional evening among his fellows at the Royal Society Club, or at the gatherings of the Royal Society, had a wonderfully clear intelligence and an astonishingly penetrative insight. No man ever more justly earned the title of philosopher. He was not so prolific or so diffuse as Priestley, but his learning was infinitely deeper and broader, and there is not a single branch of the science of his day which he did not illumine and adorn,—chemistry, astronomy, optics, mechanics, acoustics, mineralogy, crystallography, botany, physiology, pathology,—each in turn was the subject of his intellectual activity. It is, however, only with his chemical work that we have here to do. Reference has already been made to the part which Wollaston's paper, "On Super-acid and Sub-acid Salts," played in securing attention to the atomic theory; his "Synoptical scale of chemical equivalents" was of special service to the student and the manufacturer in facilitating the application of the laws of chemical combination to operative chemistry. His "Description of a reflective Goniometer" is a classic in the literature of chemical crystallography, and marks an epoch in the history of that subject. His discovery of a process by which platina may be rendered malleable proved of incalculable service to practical chemistry and the arts. Some idea of what that service has been may be gained by recalling what we have secured, and secured only by our crucibles and other vessels of platinum, and by the use of platinum foil and wire, and by imagining what our position would be if we were wholly deprived of these articles. Platinum had been known for some sixty years before Wollaston's time, but, as has been stated, "the very properties which made its value certain if it were wrought into vessels, forbade its being easily fashioned into them," and whole cargoes of the native metal are said to have lain unpurchased for years in London, as it could not be turned to account. Wollaston, foiled in his attempts to make a living by medical practice, became, as is well known, rich by his process of working platinum, which he carried on in secret and with the aid of a faithful old servant in his laboratory, a small detached building at the bottom of his garden, in Hunter Street, Brunswick Square.

In the early part of the century the price of manufactured platinum was less than half its present value. In 1805 platinum crucibles were to be obtained from Mr. Carey, 182, Strand, at 17s. 6d. the ounce, whilst wire was 16s. At the time of the foundation of the Chemical Society, the price of manufactured platinum had more than doubled.

Wollaston first made known his process in the Bakerian Lecture of 1828—the year of his death—and the Council

of the Royal Society "deemed themselves bound to express their strong approbation of this interesting memoir by awarding a Royal medal to its author, and they anticipate with confidence a general approbation of what they have done." The further development of the metallurgy of platinum in this country is associated with the firm of Johnson, Matthey, and Co., who worked platinum for many years before any other commercial manufactory was established. The process of Wollaston appears to have been first worked, sometime between 1800 and 1808, by Mr. Thomas Cock, a relative of Mr. Percival Johnson, who began the refining and manufacture of platinum in Hatton Garden.

Wollaston's name is further connected with the platinum group of metals by his discovery of rhodium, which he published in 1804, immediately after the existence of iridium and osmium had been announced by Smithson Tennant, and also by his discovery of palladium. The manner in which the last-named metal was made known constitutes one of the most singular episodes in the history of scientific discovery, and affords a curious commentary on certain phases of Wollaston's character. In fact, one or two points in Wollaston's connection with the discovery and working of the platinum metals are somewhat obscure.

In 1803 appeared an anonymous circular which was sent to a number of persons, amongst them the editors of *Nicholson's* and *Tilloch's Journals*, stating that a new metal—palladium or new silver—could be purchased from Mrs. Forster, 26, Gerrard Street, Soho, in samples of 5s., half-a-guinea, and 1 guinea each, the price being at the rate of 1s. per grain. Certain of the properties of palladium were given in the advertisement to show that it was "a new noble metal." This announcement attracted the attention of Chenevix, an Irish gentleman, well known as a Fellow of the Royal Society, and for his analyses of certain minerals and for his work on oxygenised and hyper-oxygenised muriatic acid. The mode adopted to make known a discovery of so much importance, without the name of any creditable person except the vendor, appeared to Mr. Chenevix unusual in science and not calculated to inspire confidence. Accordingly, with a view to detect what he conceived to be an imposition, Mr. Chenevix procured a specimen and eventually the whole quantity which had been left for sale with Mrs. Forster, who, she stated, was totally unacquainted with the person who brought the metallic substance and the printed paper to her house. Chenevix found all the statements in the paper to be correct with the exception of that of the specific gravity, which he stated to be different by 1 or 2 per cent. He made a long and elaborate investigation of the matter, and concluded that the pretended new metal was a combination of platinum and mercury. He sent in his memoir to the Royal Society, and two evenings were spent in the reading of it.

The Journal Book of the Society, the entries of which were made under the direction of the Secretaries, if not actually by them, gives a *précis* of this paper. We read: "Thus, after having been baffled in his attempts to discover, by analysis, the component parts of this substance, which he (the author) could never bring himself to consider as a new metal, a synthetic process at length led him to the discovery that the whole pretence was an imposition, and that the substance is, in fact, a combination of platina and mercury; in which the latter, while it masks the most characteristic properties in the former, loses the greater number of its own distinctive qualities."

"The singular fact that an alloy of two metals should be produced, the specific gravity of which is little more than one-half of what it ought to be by calculation, is, no doubt, worthy of particular attention; and as quicksilver was in this process brought to a fixed state under circumstances never before observed, a notion might be entertained that the great desideratum in alchemy, the fixation of mercury, was by no means a visionary object. . . . Those who cultivate chemistry with any degree of ardour

will be gratified to see in this paper the pains taken by the author, and the various modes he has devised, to produce this compound metal in its most perfect state of combination."

A few months later, the editors of the various scientific periodicals received "under cover of the twopenny post," an unsigned paper offering a reward of £20 for the artificial production of palladium. The editor of *Nicholson's Journal* says the paper "is written in the same hand as a note which covered a small piece of palladium mentioned to have been received by me last midsummer. Upon inquiry, I find that Mrs. Forster has received the sum of £20 with instructions conformable to this paper. The paper ran as follows:—

December 16, 1803.

"SIR,—As I see it said in one of your journals, that the new metal I have called palladium, is not a new noble metal, as I have said it is, but an imposition and a compound of platina and quicksilver, I hope you will do me justice in your next, and tell your readers I promise a reward of 20£ now in Mrs. Forster's hands, to any one that will make only 20 grains of real palladium, before any three gentlemen chymists you please to name, yourself one if you like.

"That he may have plenty of his ingredients, let him use 20 times as much quicksilver, 20 times as much platina, and in short of anything else he pleases to use: neither he nor I can make a single grain.

"Pray be careful in trying what it is he makes, for the mistake must happen by not trying it rightly.

"My reason for not saying where it was found, was, that I might make some advantage of it, as I have right to do.

"If you think fit to publish this, I beg you to give the names of the umpires, as I have desired Mrs. Forster to keep the money till next midsummer, and to deliver it only in case they can assure her that the real metal is made by a certificate signed by you, and by them, on this check.

"I hope a little bit of whatever is made may be left with Mrs. Forster."

Mr. Nicholson nominated Hatchett and Edward Howard to join himself as judges of the product which might be made in their presence; but the £20 was never claimed, and in 1805, Wollaston, in a memoir contributed to the *Philosophical Transactions*, announced that he was the discoverer of the new metal, to which he had given the name palladium; "from the planet which had been discovered, nearly at the same time, by Dr. Olbers."

What was Wollaston's motive in bringing his discovery to the notice of the scientific world in so extraordinary a manner can only be surmised. From the account of his memoir given in the Journal Book of the Society, in which no mention is made of Chenevix and his work, he refers to the "concise delineation of its character" given in the advertisement of the metal, in which he says he "avoided directing the attention of chemists to the source from where it had been obtained, and thereby reserved to himself a more deliberate examination of many phenomena that yet remained unexplained in the analysis of platina, by which he was subsequently led to the discovery of rhodium." No proper explanation was given of the circumstance that he, as Secretary of the Society, allowed Chenevix's paper to appear in the *Transactions*: It must have been his duty actually to read this paper at the two meetings when it was brought before the Fellows; he must also have been responsible for the account which appears in the Journal Book, and which, as one now peruses it, in the light of what subsequently happened, is almost cutting in its sardonic humour and irony. It has been stated that Wollaston did all in his power to persuade Chenevix to withhold or withdraw his paper. Be this as it may, there is no doubt that Chenevix keenly felt the humiliation he suffered. He retired to the Continent, and all his subsequent papers were published in France.

(To be continued).

NOTICES OF BOOKS.

Calculations on Analytical Chemistry. By EDMUND H. MILLER, Ph.D. London and New York: Macmillan and Co., Ltd.

DR. MILLER, of Columbia University, has written a textbook for the use of students in schools and colleges. His aim has been to explain clearly the principles involved in making the various calculations required in analytical chemistry, and we think that no one who has thoroughly grasped the principles as set forth and illustrated in this work should be at a loss in performing similar calculations however complex the material with which they are dealing.

The work consists of ten chapters and a score of tables. Chapter I. explains the method of obtaining the chemical equivalent of an element and how from this the atomic weight may be determined. The following seven chapters deal with the methods of analysis of compounds and mixtures in the three states, whilst the ninth is devoted to the consideration of the heat absorbed or set free by chemical reactions, and the last chapter deals with electrochemical equivalents.

More than 200 examples are given throughout the work; many are fully worked out in the body of the work, the remainder being placed at the ends of the chapters to enable the student to test his knowledge. We have verified many of the examples, and the only error we could

detect was on p. 126, line 14, where $\frac{20000}{10}$ should be $\frac{20000}{10-1}$.

History of Chemistry, since the time of Lavoisier. By Dr. A. LADENBURG. Translated from the second German Edition by L. DOBBIN, Ph.D. With additions and corrections by the author. Edinburgh: The Alembic Club, William F. Clay. 1900. Pp. 373.

THE science of chemistry assumed a new aspect in the hands of Lavoisier, and it is for this reason that the author has not gone back further for the starting point of this history.

Before the time of Lavoisier the "phlogiston" theory was the accepted one of chemists, but shortly after the discovery of oxygen, Lavoisier repeated the experiments of Priestley and Scheele, but drew conclusions from them totally different to those of the two other chemists. He at once recognised oxygen as that part of the air which unites with the combustible matter during its combustion, and some time afterwards, in the year 1777, he advanced a complete theory of combustion in which he says:—"1. Heat and light are disengaged in every combustion. 2. Substances burn only in pure air. 3. This is used up in the combustion, and the increase in weight of the substance burned is equal to the loss in weight of the air. 4. The combustible substance, by its combination with pure air, is usually converted into an acid; the metals, on the other hand, are converted into metallic calces."

Lavoisier adheres to Boyle's definition of an element, and this definition is retained to the present day. He, however, not only overthrew the old "phlogiston" theory, but he introduced a new one in its place, the principal points in which are his statement, that in all kinds of chemical reactions it is the kind of matter alone that is changed, whilst its quantity remains constant; that all acids contain oxygen united, as he expresses it, with a basis or a radical, and the combustion theory referred to above.

We have dwelt rather long on Lavoisier's work as it marks an important epoch in the development of modern chemistry. Many other writers and thinkers have followed him and gradually brought the science up to its present form. Dalton's atomic theory was another great advance, as also was the inception and development of the radical and the nucleus theories.

All this and much more is fully discussed and analysed in these interesting pages. Chapter XVI., the last, has been specially written for this English edition, and treats of the development of chemistry during the last fifteen or twenty years. This latter development is distinguished by the increasing prominence of physical or general chemistry. To this end such workers as Horstmann, Gibbs, Van der Waals, and van 't Hoff have largely contributed.

Again, Moissan on the one hand, and Dewar on the other, have achieved great scientific results, the one in his work on very high temperatures, and the other in the production of extreme cold.

Our knowledge of the composition of the atmosphere has also been much extended owing to the labours of Lord Rayleigh and Professor Ramsay, while the development of the chemistry of the carbon compounds has advanced to an unexpected extent.

What the coming phases of the science may be, nor how our present ideas will appear to future investigators, none can foretell; but as a history of what chemistry has been during the last 130 years, this book is of great service, and deserves the success it has achieved.

Laboratory Note-book for Chemical Students. By VIVIAN B. LEWES and J. S. S. BRAME. London: Archibald Constable and Co. Pp. 170.

WE are glad to come across a laboratory note-book such as this, which has been compiled, not with reference to any particular syllabus or examination, but to cover such practical work as a student should be familiar with if he is to have a good ground-work in the subject of practical chemistry. By omitting long descriptions of such simple matters as filtration, weighing, &c., which often fill up many pages, the authors have been enabled to include all the principal reactions of the metallic and acid radicals, besides the preparation of gases, &c., and some of the more simple quantitative experiments. In Part II. we find the usual tables given for the group separation of the bases, and a general scheme for the analysis of mixtures. Part III. is devoted entirely to experiments of a quantitative character, and includes the simple examination of water, fuels, lubricating oils, and explosives, these latter being more especially needed by students desirous of entering the army or navy. The book is plentifully interleaved with blank sheets for the student's own notes, working out equations, &c., the whole making a welcome addition to this class of literature.

The Measurement of High Temperatures. ("Mesure des Températures élevées"). By H. LE CHATELIER and O. BOUDOUARD. Paris: G. Carré and C. Naud. 1900. Pp. 220.

THE first to take up the measurement of high temperatures was Wedgwood, the celebrated Staffordshire potter, and in the year 1782 he constructed and used a pyrometer in which he utilised the contraction of clay; this pyrometer was the only one in use for nearly a century.

Since Wedgwood's time many savants have been engaged in the study of the measurement of high temperatures with varying success. As a few examples of the kinds of thermometers used for high temperatures we may mention the following:—Wedgwood's, which registers by the permanent contraction of clay; Pouillet's, by the dilatation of air; and Siemens's, by the alteration of electric resistance of platinum.

The authors first consider the normal scale of temperatures, that is the thermo-dynamic scale; but as it is impossible to utilise this with accuracy, it becomes necessary to have a practical scale, in a similar manner to the

actual metre rod which is kept as a standard at the Bureau International des Poids et Mesures. This practical scale exists as a hydrogen gas thermometer of constant volume charged with hydrogen at a pressure of 1000 m.m. of mercury at the temperature of melting ice, but with high temperatures it is not possible to get closer results than 1°, and practically even greater differences occur.

Electric pyrometers have enabled us to determine a large number of temperature points, concerning which our ideas were very vague, and it is with this instrument that M. Osmond, Sir William Roberts-Austen, M. Charpy, and others have carried out their researches on the molecular transformations of irons and steels.

Pyrometers for measuring calorific radiations are also described, as well as those by which high temperatures may be estimated by means of luminous radiations; these are similar to those last mentioned, with this difference that they only use the visible rays, and not the invisible or heat rays; it is by these means that the highest temperatures of all can be measured.

The authors have handled the subject with great ability, and have produced a really excellent work on this subject.

The Photographer's Note-book and Index. By Sir DAVID SALOMONS, Bart., M.A. London: Marion and Co.

THIS useful note-book has been revised, and much new matter added. It contains a lot of information and rules in a compact form, for taking, printing, and enlarging photographs, &c., and a number of ruled pages for entering the details of conditions under which the photographs were taken, such as length of exposure, developer used, &c.

A Treatise on Crystallography. By W. J. LEWIS, M.A. Professor of Mineralogy in the University of Cambridge. Cambridge: The University Press. 1899. Pp. 612.

THE author has set out clearly in this volume the views held at the present time as to the classification of crystals and the principles of symmetry on which the classification is based; his treatment of the subject has been as far as possible geometrical, and, with the exception of the formulæ of plane and spherical trigonometry necessary for the solution of triangles, very little analysis has been introduced into the main discussion.

By the principles laid down and the relations established in the earlier chapters the classification of crystals is rendered easy, and it is shown that there are only thirty-two classes possible, and these classes are arranged in seven larger groups known as systems. It is now generally held that each of the thirty-two possible classes of crystals is a definite group, the forms of which are a direct consequence of the elements of symmetry present in it. The names adopted by various authors for the systems and classes differ considerably; Professor Lewis has generally adopted Miller's names for the systems, but he also gives some of the synonyms employed by other crystallographers. The systems and the classes included in each system are fully developed in Chapters XI. to XVII.; these are followed by a chapters on twins and other composite crystals.

Twin crystals can be divided into two main classes according to the manner in which the parts are united; these are: 1. Juxtaposed twins in which the portions are united along a plane surface, and lie on opposite sides of it; and 2. Interpenetrant twins in which the portions are intimately mingled without any regular surface of separation between their matter. Chapter XX., and last, deals with the goniometer, the different forms of which are fully described and illustrated.

The diagrams in a work of this class are of considerable importance, as good figures are great aids to the understanding of the geometrical relations of crystals. We

must congratulate the author on the excellence of the diagrams, which appear throughout to have been most carefully prepared.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 17, April 23, 1900.

Heat of Combustion and Formation of Iodine Compounds.—M. Berthelot.—The author employs the calorimetric bomb and compressed oxygen to determine the heat of combustion and heat of formation of iodine compounds. He finds that the iodine is liberated without any sensible formation of hydriodic or iodic acids. Such compounds as iodoform, CHI_3 , and periodioethylene, C_2I_4 , which are rich in iodine, burn easily and entirely in compressed oxygen. By this method he is able to employ considerable quantities of the compound, even as much as 8 grms. in certain cases, and so ensure precision of the determinations. Numbers were found for methylodihydric ether, CH_2I , methylene iodide, CH_2I_2 , iodoform, CHI_3 , ethyliodohydric ether, $\text{C}_2\text{H}_5\text{I}$, normal propyliodohydric ether, $\text{C}_3\text{H}_7\text{I}$, isopropyl iodide, $\text{C}_3\text{H}_7\text{I}$, allyl iodide, $\text{C}_3\text{H}_5\text{I}$, iodobenzene, $\text{C}_6\text{H}_5\text{I}$, iodobenzoic acid, $\text{C}_7\text{H}_5\text{IO}_2$, iodosalicylic acid, $\text{C}_7\text{H}_5\text{IO}_3$, di-iodosalicylic acid, $\text{C}_7\text{H}_4\text{I}_2\text{O}_3$, ethylene iodide, $\text{C}_2\text{H}_4\text{I}_2$, di-iodoform and iodoform, CHI_3 .

New Indicator for Acidimetry and its Application to the Estimation of Boric Acid.—Jules Wolff.—The author uses as an indicator ferrous salicylate in a solution of sodium salicylate. A solution of boric acid added to a given volume of sulphuric acid of known strength coloured with the new indicator, changes colour at the precise moment of saturation of the sulphuric acid by the standard soda solution, from violet to orange, the latter tint persisting in presence of excess of alkali. When the sulphuric acid is in great excess, the addition of the indicator at first produces no colouration, but the colour comes as the neutralisation of the acid proceeds. The author obtains the indicator in a crystalline state. He finds that it is very sensitive in presence of alkaline bases, also in the presence of sulphuric, nitric, hydrobromic, hydriodic, and hydrochloric acids. In presence of phosphoric and hydrofluoric acids the violet colour is not produced.

Selenides and Chloro-selenides of Lead.—M. Fonze-Diacon.—The author prepares crystalline selenide of lead (1) by the reduction of the selenate under the influence of hydrogen or carbon; (2) by the action of hydrogen selenide on the vapour of lead chloride; and (3) by direct fusion, in the electric furnace, of precipitated lead selenide. He was unable to prepare the sub-selenide, but succeeded in preparing, both by the wet and dry method, a chloro-selenide of lead.

The Alkaline Selenio-antimonites.—M. Pouget.—Little is known of the compounds of antimony selenide with the alkaline selenides. Two compounds only have been described:— $\text{SbSe}_4\text{Na}_3 + 9\text{H}_2\text{O}$ and $\text{SbSe}_3\text{SeNa}_3 + 9\text{H}_2\text{O}$. The author succeeds in preparing several other selenio-antimonites by a method identical with that used for the preparation of alkaline sulphantimonites, i.e., by the action of antimony selenide on dissolved alkaline selenides. Among these are $\text{Sb}_2\text{Se}_3 + 3\text{K}_2\text{Se}$, $\text{SbSe}_3\text{Na}_3 + 9\text{H}_2\text{O}$, $\text{Sb}_2\text{Se}_5\text{K}_4 + 2\text{SbSe}_3\text{K}_3 + 4\text{H}_2\text{O}$.

Micro-chemical Researches on Yttrium, Erbium, and Didymium.—E. Pozzi-Escot and H. C. Couquet.—The following reactions allow of the identification of yttrium, erbium, and didymium:—(1) Salts of yttrium give, with chromate of ammonium, an yttria chromate

which crystallises, after some minutes, in the form of voluminous hexagonal elongated crystals, slightly tinted violet. (2) Yttrium salts give, with a solution of chromic acid in concentrated sulphuric acid, small crystals, which, after a time, become transformed into voluminous crystals (Couquet's reaction). (3) Erbium salts give, with ammonium chromate, a compound which either does not crystallise at all, or else does so with great difficulty. (4) Erbium salts give, with Couquet's reaction, large badly-defined crystals. (5) Didymium salts give, with ammonium chromate, a didymium chromate formed in large orange prismatic crystals. (6) Didymium salts give, with Couquet's reaction, an amorphous precipitate, which, after some time, crystallises in prisms often split in the form of stars. (7) Chlorides of yttrium, didymium, and erbium give, with palladium chloride, characteristic double chlorides.

No. 18, April 30, 1900.

Manganous Fluoride.—Henri Moissan and M. Venturi.—Manganous fluoride, MnF_2 , can be easily prepared in the state of a crystalline sand by the action of hydrofluoric acid on manganese. This substance may also be obtained in beautiful crystals by utilising the property it possesses of dissolving in melted manganese chloride. Manganous fluoride is insoluble in water, alcohol, and ether, so differing entirely from the chloride. It is a compound easily reduced both by metals and non-metals, giving, in many cases, crystalline products as a result of the decomposition. It is easy to add fluorine to the compound, and so prepare the crystalline sesquifluoride of manganese, MnF_3 .

Samarium.—Eug. Demarçay.—Samarium prepared by the crystallisation of the double magnesium nitrites, as already described by the author, can be obtained in a state of comparative purity, showing after continuous fractionation the properties of the first and last portions to be absolutely identical, both with regard to the absorption and the spark spectrum. The absorption spectrum obtained by the author coincides in almost all respects with that previously published by Lecoq de Boisbaudran. The line 614.4 is, however, quite absent in this specimen of pure samarium. The author obtained the atomic weight of his samarium by the synthesis of the sulphate from samaria and sulphuric acid, varying between 147.2 and 148. Nitrate of samarium and magnesium, $\text{Sm}(\text{NO}_3)_2 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, is a pale yellow salt, crystallising in large rhombohedra and melting between 93.5° and 94.5°. The simple nitrate, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, is formed in large orange-yellow crystals melting at 78–79°, and is very hygroscopic.

Compounds of Metallic Iodides with Sulphurous Anhydride.—E. Péchard.—When sulphur dioxide is allowed to pass into a solution of potassium iodide, the latter acquires a yellow tint, becoming orange-coloured if the solution is concentrated. This colouration is not due to the liberation of iodine. Solid potassium iodide which has been carefully dried absorbs also large quantities of sulphur dioxide and becomes yellow. Both the solid and the solution lose the absorbed gas by the action of heat. The author finds, therefore, a dissociable compound of potassium iodide and sulphurous anhydride. He first determines the dissociation tensions at different temperatures between 0° and 30°. An analysis of the compound shows that it probably has the formula $\text{SO}_2 \cdot \text{KI}$. Other soluble iodides form analogous combinations, those of sodium, ammonium, barium, and calcium having been prepared.

Bromination by means of Aluminium Bromide.—Ch. Pouret.—By allowing aluminium bromide to act on the chlorine derivatives CCl_4 , C_2Cl_4 , C_2Cl_6 , the corresponding bromine derivatives are formed, CBr_4 , C_2Br_4 , C_2Br_6 . This operation takes place in a glass bulb or in sealed tubes; in the latter case the yield is as large as 90 or 92 per cent. By using powdered aluminium on the same chlorides in presence of bromine, the author obtained in all cases C_2Br_6 .

Gases emitted from the Mont-Dore Springs.—F. Parmentier and A. Hurion.—After collecting the gas from the spring, the authors used potash solution, and found that from 100 c.c. about 0.5 c.c. remained unabsorbed. This residue showed negative properties. Analysis of the gas gives the following result:—

Carbonic acid	99.50
Nitrogen	0.49
Argon	0.01

100.00

Action of Monochloroacetic Ethers on Sodium Acetylacetone.—F. March.—Bischoff, making use of the property possessed by bodies having a group CH_2 placed between two CO groups, of reacting with the halogen compounds of saturated hydrocarbides, investigated the action of monochloroacetic ether both on sodium acetylacetic ether and on sodium malonic ether. He obtained by this means the acetyl succinic ether and the ethenyl-tricarballic ether. Haller and Barthe, by allowing monochloroacetic ether to react on sodium cyanacetic ether, prepared a mixture of cyanosuccinic and cyanotricarballic ethers. The author finds that sodium acetylacetone reacts in the same way with monochloroacetic ether.

Action of Ethylidene Chloride on Phenols.—R. Fosse and J. Ettlinger.—The authors investigate the action of ethylidene chloride on acetal of orthocresol; acetal of paracresol, and resorcine.

Presence of Tyrosine in Waters of Contaminated Wells.—H. Causse.—An examination of the water shows that when it is coloured yellow by chloromercurate of para-diazo-benzene sulphate of sodium, tyrosine is present. The circumstance that the intensity of colouration increases with the disappearance of ammonia and the clearness of the water, shows that the tyrosine did not pre-exist, but appears to be due to an energetic oxidation which has a simultaneous effect on the mineral and organic substances present in the water.

MISCELLANEOUS.

Proposed University of Birmingham.—The report of the Advisory Committee as to the technical and commercial sections of the University of Birmingham has recently been issued. The committee have visited a number of Colleges and Universities, both at home and abroad, and have also had interviews with many of the leading manufacturers in the city and district, with a view to ascertaining the peculiarities of the industries with which they are associated and the best means of meeting their needs, also the kind of technical knowledge desirable in the members of their staff. They have classified the industries of the district as follows:—1. Mining. 2. Metallurgy. 3. Engineering. 4. Chemical trades. 5. Non-metallic trades; and they recommend that there shall be chairs of Mining, Metallurgy, Engineering, and Applied Chemistry. The cost of the land, buildings, &c., for carrying out all the recommendations detailed in this report is estimated at £155,000, and the cost of maintenance (including the staff) at £10,450 per annum. A very important recommendation, which may not perhaps find favour with the staff, is that to properly carry out the necessary courses the usual vacations be considerably shortened, and the time of the students more fully occupied. The staff would also be expected to give their whole time to the service of the College, and should not be expected to assist their incomes by outside work. We are afraid that the salaries required by first-class men if such conditions were rigidly enforced would be prohibitive.

Merck's Digest, No. 7.—This number of the *Digest* contains an account of the two halogenised fats *iodipin* and *bromipin*. These products are obtained by the addition of iodine and bromine respectively to oil of sesame, or teel oil (from *Sesamum orientale*). They are yellowish liquids of a purely oily taste, and possess the physical properties of fatty oils. Iodipin is supplied commercially as a 10 per cent and a 25 per cent preparation, and bromipin is supplied at 10 per cent and 33½ per cent strengths, the latter in capsules. These two preparations have been the subject of comprehensive physiological and clinical experiments which show them to be efficient substitutes for the usual iodine and bromine preparations, especially the alkaline iodides and bromides, and free from their objectionable secondary properties.

The Preparation of Acrolein.—A. Wohl and L. Neuberg.—The author advantageously replaces the bisulphate of potassium, in the preparation of acrolein, with boric anhydride, or even with ordinary boric acid. To obtain the acrolein, 500 grms. of glycerin mixed with 335 grms. of crystallised boric acid are distilled in a metal retort of 3 litres capacity; this is first heated without the cover so long as steam comes off, and until the mass commences to turn black. It is then allowed to cool, the cover is then placed on the retort, which is heated strongly after having surrounded the apparatus with asbestos card. The distillation is finished after about three-quarters of an hour, and 154 grms. of acrolein are obtained, that is 50.5 per cent of theory. If the temperature is not sufficiently high at the commencement, the distillation will be too slow, and boric acid will be deposited in the cool part; this may cause disagreeable obstructions. The raw acrolein obtained in this manner is purified by distilling two or three times over chloride of calcium. — *Berichte*, xxii., p. 1352.

MEETINGS FOR THE WEEK.

- MONDAY, 28th.—Society of Arts, 4.30. "Imperial Telegraphic Communication," by Sir Edward Sassoon, M.P.
TUESDAY, 29th.—Royal Institution, 3. "Ruskin, Man and Prophet," by R. Warwick Bond, M.A.
WEDNESDAY, 30th.—Society of Arts, 8. "Russian Central Asia—Countries and Peoples," by A. R. Colquhoun.
THURSDAY, 31st.—Royal Institution, 3. "Chaucer," by the Rev. Canon Ainger, M.A., LL.D.
FRIDAY, June 1st.—Royal Institution, 9. "Bunsen," by Sir Henry Roscoe, F.R.S., &c.
SATURDAY, 2nd.—Royal Institution, 3. "The Growth of Chamber Music" (with Musical Illustrations), by Sir Frederick Bridge, Mus. Doc.

The CORPORATION OF HALIFAX are prepared to receive applications for the post of CHEMIST at their GASWORKS. Applicants are to state in full their training, experience, present position, and salary required, accompanied by recent testimonials as to character, industry, and ability. — Applications to be endorsed "Chemist" and addressed to the undersigned on or later than May 31st, 1900.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2114.

RADIO-ACTIVITY OF URANIUM.*

By Sir WILLIAM CROOKES, F.R.S.

1. THE researches of M. Henri Becquerel have shown that compounds of uranium possess the property now called radio-activity; that is, rays emitted by them affect a sensitive photographic plate through bodies usually considered opaque to light; they discharge an electrometer when brought near it; and they are deflected by a magnet. These rays are now called "Becquerel rays," or "uranic rays."

2. On the discovery by M. and Mme. Curie of polonium and radium, bodies of enormous radio-active powers, it was suggested that uranium might possibly owe its power to the presence of a small quantity of one of these bodies. But in a paper published in the *Revue Générale des Sciences* for January, 1899, Mme. Curie says:—"This does not appear probable, for if such were the case different samples of uranium compounds would have very different radio-activities, but in the course of a number of experiments made with various samples of metallic uranium, as well as with oxides and salts from various sources, I have never found any marked difference between the relative activities of the same compound."

In another paper (M. and Mme. Curie, *Comptes Rendus*, cxxvii., p. 175; *CHEM. NEWS*, lxxviii., p. 49, July 29, 1898), the same author says that "the property of emitting rays . . . which act on photographic plates is a *specific property of uranium and thorium*." "The physical condition of the metal seems to be of an altogether secondary importance." "Uranium and thorium alone are practically active."

3. When the discovery of radium was announced, and it was said to have "to all appearance the properties of almost pure barium" (M. and Mme. Curie and M. Bémont, *Comptes Rendus*, cxxvii., p. 1215; *CHEM. NEWS*, lxxix., p. 1, January 3, 1899), it occurred to me that radium might be found in detectable quantities in some barium minerals were search made among them from different localities. Accordingly specimens of the following minerals were put on sensitive plates, a sheet of black paper separating them from the sensitive surface. As it was probable that the radio-active substance would be present, if at all, in very minute quantities, the sensitive plate was exposed to their influence for forty-eight hours.

Barytes (Heavy Spar).

- " from Hungary. (Three specimens).
- " " Cumberland. (Eight).
- " " Westmoreland. (One).
- " " Cumberland. (A fine crystal).
- " " Derbyshire. (Three).
- " " Arkendale. (One).
- " " Hartz. (One).
- " " Scotland. (One).
- " " Ireland. (Two).
- " " Northumberland. (Two).
- " " Arran. (One).
- " " Cherbourg. (One).
- " " Several unnamed, but finely crystallised, specimens.

Witherite from Lancashire. (One).

" " Cumberland. (Four).

" " Northumberland. (One).

Not one of these minerals showed the slightest action on the sensitive plate.

4. Having obtained negative results with barium compounds, I went through every mineral in my cabinet—a somewhat extensive collection, numbering many fine specimens. Large photographic plates were covered with black paper, and the minerals were laid on them as close as they could conveniently be placed, accurate note of their names and positions being recorded. They were exposed in total darkness for forty-eight hours. By this means a list of radio-active minerals was ultimately obtained. They were then tested for order of intensity of action. The following is a list of active minerals arranged in order, the most active heading the list:—

1. Pitchblende.
2. Uranite.
3. Autunite.
4. Orangite.
5. Thorite.
6. Euxenite.
7. Samarskite.
8. Alvalite.
9. Broggerite.
10. Monazite.
11. Xenotime.
12. Arrhenite.
13. Sipilite.
14. Fergussonite.
15. Chalcocite.
16. Hiemite.

It will be observed that these minerals all contain either uranium or thorium.

5. Pitchblende was the most radio-active mineral, but it varied much in different parts. A slice was cut from a piece of pitchblende from Cornwall and the surface was polished. A sensitive photographic plate was pressed against it, and after twenty-four hours the plate was developed. The impression showed the structure of the mineral in a remarkable manner, every little piece of pitchblende showing black, those portions in which the radio-active substance was not so operative showing in half tint, while the felspar, quartz, pyrites, &c., having no radio-activity, left the plate transparent.

Pitchblende from different localities differed greatly in action.

6. A large crystal of orangite from Arendal was ground flat and polished at one end and side, and a piece of sensitive celluloid film, cut half through so as to allow it to bend sharply, was put on the polished surfaces, one half pressing against the end and the other half against the side. The exposure was continued for seventy-two hours. On developing, no difference could be seen in the intensity of the impression, whether made by the end or the side of the crystal. The impression also was uniform over the surface, the cracks in the surfaces not having impressed themselves.

These experiments were repeated with the interposition of a thin sheet of celluloid between the mineral and the sensitive plate. The results were practically the same as before.

7. Roughly speaking, the action of pitchblende is in proportion to the percentage of uranium in the mineral. Finely powdered pitchblende of different degrees of richness were experimented with. Cells were made of thick lead pipes half an inch internal diameter and one inch long, closed at the lower ends with card. They were filled with powdered pitchblende, one containing 43 per cent U_3O_8 and the other 12 per cent U_3O_8 . A sensitive plate being covered with black paper, the lead cells were laid on it and kept in total darkness for 120 hours. The intensity of the spot under the 43 per cent ore on development was found to be at least three times that of the one under the 12 per cent ore.

Two lead cells were taken, one being a quarter of an

* A Paper read before the Royal Society, May 10, 1900.

inch long and the other two inches long. They were filled completely with the 43 per cent ore, and a sensitive plate exposed to their action for forty-eight hours. On developing it was doubtful whether any difference existed in the intensity of the two spots, proving that the action does not pass through much thickness of active material, a quarter of an inch being equal in effect to two inches.

No difference in the action was noticed when the bottom of the cell was made of thin glass cemented on, instead of card.

Four cells were filled with pitchblende and placed side by side on a sensitive plate. After having acted twenty-four hours the first was removed, the second after forty-eight hours, the third after seventy-two hours, and the last was kept on for ninety-six hours. On developing the plate the spots had intensities varying with the lengths of exposure, and in about the right proportion, on the assumption that double the time of action gives double the intensity of blackening.

8. For convenience of comparison I had a number of glass cells made, three quarters of an inch wide and deep, so that they could either be sealed up or closed with a cork. A piece of apparatus was made so as to take radiographs of samples with more ease and certainty. A lead plate, 2 m.m. thick, $6\frac{1}{2}$ inches long, and $2\frac{1}{4}$ inch wide, has circular holes punched in it, one inch in diameter. Under the thick plate of lead is another thinner plate, made of pure assay foil, and having holes in it, concentric with the others, but barely $\frac{3}{4}$ inch in diameter, so that one of the small cells will not pass through the lower hole, but will pass easily through the upper hole, and thus be kept in place. To prevent contact between the lead plate and the sensitive surface a thin sheet of celluloid is fixed beneath, with holes punched in it concentric with those in the lead plates. In the top left corner of the lead plates is a short steel pin, which can be pressed on the sensitive plate and so register its position in respect to the cells experimented with. The lead and celluloid plates are then bound together and the whole is fitted into a shallow wooden tray with a light-tight cover.

A sensitive film is laid face upwards at the bottom of the wooden tray; on this are put the lead screens, and then the experimental cells of radio-active bodies in order, careful note being taken of their relative positions.

9. Wishing to prepare compounds of radium and polonium, the very curious bodies discovered by M. and Mme. Curie, I arranged with my friend Mr. Tyrer, Stirling Chemical Works, for the systematic working up of half a ton of pitchblende. It was necessary to examine every precipitate and filtrate in each stage of the operation, and for convenience of registration they had to be compared with a standard cell filled with a substance unvarying in action. After many trials, I selected crystallised uranium nitrate as being strongly radio-active and easily prepared pure. This led me to the observation which forms the subject of the present paper.

10. The following compounds of uranium were tested simultaneously, being put into glass cells and arranged on a lead screen with seven holes:—

1. Metallic uranium, from M. Moissan.
2. Uranium nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.
3. Uranium acetate.
4. Uranium persulphate.
5. Uranium protosulphate.
6. Uranium oxide (green), UO_2UO_3 .
7. Uranium oxide (black), UO_2UO_3 .

For twenty-four hours the sensitive plate was exposed to the influence of these bodies. With the exception of metallic uranium, which showed least action, there was not much difference between the effect produced by any of the others.

11. In order to prepare uranium nitrate of great purity for a standard, I took some pounds of the commercial salt and purified it, first by solution in ether (13), and then

by repeated crystallisation. After many operations a cell was filled with the crystals, and it was used as a standard. To my surprise, after having acted on a sensitive plate for twenty-four hours, on development not a trace of image could be seen.

12. Thereupon I tried the following experiments to ascertain if the great radio-activity of some uranium compounds and the absence of it in others might be caused by some variation of physical, crystalline, or chemical condition.

Commercial uranium nitrate was taken, and—

(1) A portion was heated with excess of nitric acid to dryness on the water-bath. It was powdered and put in a cell.

(2) A similar portion of the salt was dissolved in alcohol, and the solution evaporated to dryness over the water-bath. The resulting orange-coloured pasty material was ground and put in a cell.

(3) The salt was treated in the same way as No. 1, except that the excess of water and acid were not driven off.

(4) A small quantity was heated for some time on a water-bath till it was thoroughly dry. It was then powdered and put in a cell.

(5) 50 grains were put in a glass cell and heated on a water-bath to about 75°C . till it had dissolved in its water of crystallisation.

(6) 50 grains in a glass cell were heated on a sand-bath to about 230°C . The water of crystallisation having been driven off the salt fused, and on cooling remained a hard, yellow, glassy mass.

(7) A similar quantity of the same salt was heated to a little above 230°C . till it commenced to decompose.

(8) A similar quantity was heated more strongly, till about half the nitrate had decomposed.

(9) The same quantity was heated till decomposition was complete.

(10) As a standard, some of the same lot of commercial uranium nitrate from which these lots were taken was put in a cell.

These ten cells were placed in a lead screen apparatus, and a sensitive plate was exposed to their influence for twenty-four hours. On development there was not much difference between any of the impressions, that under No. 9 being a little the strongest.

Thus it appears that no modification of physical or chemical condition materially affects the radio-active property of a uranium compound when, to begin with, the salt experimented on possesses it; other similar experiments show that, starting with an inactive uranium salt, nothing that can be done to it will cause it to acquire this property. It is therefore evident that, as I had suspected, the radio-active property ascribed to uranium and its compounds is not an inherent property of the element, but resides in some outside body which can be separated from it.

Having by repeated crystallisation succeeded in preparing a photographically inactive uranium nitrate, I started experiments with several pounds of the commercial salt to ascertain the readiest means of separating from it the active body.

13. Into a stoppered cylinder I put 1 lb. of crystallised nitrate and poured on it a pound of methylated ether, sp. gr. 0.72. The salt easily dissolved on shaking, and after a few hours the whole of the crystals had disappeared, leaving at the bottom of the cylinder 1000 fluid grains of a heavy aqueous solution. I separated the aqueous solution from the ethereal solution, and evaporated it to dryness to remove traces of ether. The ethereal solution was allowed to evaporate spontaneously. Equal quantities of the soluble and the insoluble in ether I put into glass cells and added sufficient dilute nitric acid to dissolve the salt, and then evaporated each lot to dryness on the water-bath. When dry the two cells, and a third containing some of the original nitrate, were put on a sensitive plate for twenty-four hours.

On development it was found that the action of the part undissolved by ether was very strong, that of the original nitrate not more than half as strong, while no action whatever could be detected on the part of the plate covered by the salt soluble in ether.

The portion insoluble in ether, after evaporation to dryness with nitric acid, and then crystallisation in water, in no way differed in appearance from ordinary uranium nitrate. The portion soluble in ether, when dried, heated with dilute nitric acid, and crystallised, also had the same appearance as the initial salt.

14. The crystallised nitrate from the portion insoluble in ether I again extracted with ether. Most of it dissolved, and a small portion of heavy aqueous liquid settled at the bottom. As before, the nitrate which dissolved in ether had scarcely any radio-active power, while the residue from this second extraction possessed it in a strong degree. The residue after the second extraction was about double the activity of the residue after the first extraction, showing that ether, while dissolving uranium nitrate itself with facility, does not dissolve the body to which it owes its radio-activity.

15. The uranium nitrate from the portion insoluble in ether was submitted to fractional crystallisation in the following manner:—

The solution was evaporated until, on cooling, about three-fourths would crystallise out. The beaker in which this operation was performed was called No. 1. When crystallisation had finished, the mother-liquor was poured into a beaker called No. 2. A little water was added to No. 1 and it was warmed to dissolve the crystals; No. 2 was evaporated a little, and both were set aside to crystallise. When cold the mother-liquor from 2 was poured into a beaker No. 3, the mother-liquor from 1 was poured into 2, a little water being added to dissolve the crystals in 1, and the contents of the three beakers were warmed and allowed again to crystallise separately. This operation was continued as long as the uranium salt would hold out, or till the tests showed that the operations had gone far enough.

16. Tests were made to see how the operations were proceeding. A portion of the crystals from No. 1 beaker was dried and put into a cell. Some mother liquor from the last beaker was also evaporated and crystallised, and the crystals were put in a cell. The two were placed side by side on a sensitive plate and the action was allowed to proceed for twenty-four hours. On development there was no visible spot beneath No. 1 nitrate, while that beneath the nitrate from the other end of the fractionation was strong and black.

17. The crystals were removed from their cells, ignited to the green oxide, and replaced. Tested again on a sensitive plate, the results were similar to those given by the unignited nitrates. The active substance, therefore, is seen to reside in the mother-liquor.

(To be continued).

Reaction between Strychnine and Iodide of Methylene.—P. F. Trowbridge.—When heated for an hour in a sealed tube in the presence of methylic alcohol, or shaken up for several days with a chloroformic solution of the alkaloid, strychnine and iodide of methylene react one on the other, giving a white crystalline compound having the formula $C_{21}H_{22}N_2O_2 \cdot CH_2I_2$, melting at 212° . By digesting its aqueous solution with freshly precipitated chloride of silver we obtain the corresponding chlorised derivative in the form of white needles, very soluble in water, with which double salts of gold, mercury, and platinum can be prepared. The bromide can be obtained in a similar way by means of the chloride, by agitating the warm aqueous solution of the latter with oxide of silver, and slightly acidulating the filtrate with hydrobromic acid. This body appears in the form of white needles.—*Archiv der Pharmacie*, ccxxvii., p. 617.

ON THE PROGRESS OF CHEMISTRY IN GREAT BRITAIN AND IRELAND DURING THE NINETEENTH CENTURY.*

PART I.—FROM THE BEGINNING OF THE CENTURY TO THE
FOUNDATION OF THE CHEMICAL SOCIETY (1841).

By T. E. THORPE, LL.D., F.R.S.,
President of the Chemical Society.

(Concluded from p. 249).

IN the year of Davy's death, Edward Turner wrote "The Æra of Brilliant Discovery in Chemistry appears to have terminated for the present." Although the number of workers in the science was probably greater than during the first few years of the century, the volume of chemical literature actually produced, judged by the number of contributions to the various societies and to scientific periodicals, had been steadily declining during the previous ten years, and was actually not much more than half what it was in 1802. The work of the first quarter of the century had, in fact, been that of the pioneers, and it was now necessary to secure and consolidate what had been gained rather than to push on into new territory. "The time is arrived," continues Turner, "for reviewing our stock of information, and submitting the principal facts and fundamental doctrines of the science to the severest scrutiny. The activity of chemists should now, I conceive, be especially employed, not so much in searching for new compounds or new elements, as in examining those already discovered; in ascertaining with the greatest possible care the exact ratio in which the elements of compounds are united; in correcting the erroneous statements to which inaccurate observation has given rise; and exposing the fallacy of opinions which partial experience or false facts have produced." Stoichiometrical considerations were, in fact, becoming of increasing importance. The atomic theory was now a part of the settled doctrine of chemistry. To use the words of Davy, chemistry had now passed under the dominion of the mathematical sciences. The exact numerical relations of the elements and their combinations, both by weight and by volume, Prout's hypothesis and all that it implied, were types of the questions which seemed most urgently to require solution. The idea of stating the course of chemical change with a more mathematical precision than had hitherto been possible is reflected, too, in the attempts which were made at about this period to express such changes by means of equations. Chemical symbols have been used from time immemorial, but the notion of attaching a definite numerical value to them had a rational basis only after the promulgation of the atomic theory.

Berzelius is usually credited with having been the first to suggest, in principle, the system of notation at present employed by chemists, although there is a tradition in Glasgow that the merit should be ascribed to Dr. Thomas Thomson. Herschel, in his paper on "Hyposulphurous Acid," in the *Edinburgh Philosophical Journal* for 1819, uses algebraic expressions to describe the reaction between silver nitrate and calcium thiosulphate. The idea of using a mathematical notation to express the chemical composition of substances and their mutual actions, although in common use in Sweden, France, and Germany, for a time made little progress in England, partly from the conservatism of chemists, who, like Richard Phillips, failed to perceive its necessity or convenience, and to whom the language of symbols—

"... was a Babylonish dialect
Which learned chemists much affect:
It is a party-coloured dress
Of patch'd and piebald languages;
'Tis English cut on Greek and Latin,
Like fustian heretofore on satin;

and partly from the strictures of mathematicians, chief

* Presidential Address to the Chemical Society, 1900.

among whom was Whewell, who condemned the Berzelian system for what he regarded as its "gross anomalies" and "disfigurements," and its want of "mathematical symmetry and consistency"—"a system which violates mathematical propriety so entirely that it must always be disagreeable to see an example of it, for any person who has acquired the first rudiments of algebra."

Whewell, whose "forte was science, and whose foible was omniscience," of course recognised that a mathematical notation might be of the greatest service in chemistry, and, indeed, could not ultimately be dispensed with, and he made a vigorous attempt "to purify and improve the foreign system." One of the chief rocks of offence to Whewell was the method adopted by Berzelius of connecting the symbols of the elements to represent compound substances. Chemical combination is essentially an operation of addition, whereas the symbolic notation, if understood algebraically, would indicate that the constituents were multiplied by each other. There is not much force in this objection, although, as Whewell points out, we probably owe to the symbols being read algebraically the ambiguity of the words *factor* and *product*, which are sometimes used to express the ingredients producing a chemical compound by their addition, as well as the compound itself, but which in algebra properly refer to parts producing a number by multiplication. Still more objectionable to Whewell was the use of the sign $+$; this he characterised as "a wanton and superfluous violation of analogy."

Whewell's objections were rather more pedantic than practical. It was pointed out that the juxtaposition of symbols and the employment of an index figure, as practised by Berzelius, would lead the chemist into no error, because their subjects are not susceptible of algebraic powers, or of being multiplied into each other.

On general grounds, too, Whewell's system failed to commend itself to chemists, even to those who were not unmindful of the mathematical proprieties. It only approximated to mathematical consistency, and failed altogether as regards brevity and clearness. The multiplication of lines and brackets which it entailed, although algebraically just, gave a perplexing appearance to the formula, and destroyed its graphic character. The unvarying sign $+$ alternately with every letter was also objectionable. Whewell, who was not insensible to these defects in his system, suggested a method of contraction, but the compromise failed to realise the graphic perspicuity of the Berzelian notation, whilst, as an analytical expression, it was inferior to the extended system from which it was evolved. Whewell, moreover, avowedly put it forward as more suitable for the purposes of mineralogy than of chemistry, and the objection was naturally raised that a system which required new contrivances and contractions to suit different points of reasoning, and was so partial and so incomplete an expression of chemical composition in general, was certain to lead to interminable confusion and difficulty.

The serial chemical literature of the early thirties contains a number of interesting papers on chemical notation, not only by Whewell, but by Phillips, Prideaux, Warrington, and Graham, and the merits of the various systems proposed were fairly discussed, with the result that the Berzelian method was at length universally adopted. As an example of the confusion which reigned at the time, we give, from one of Phillips's papers, the composition of common phosphate of soda as expressed in the different systems of notation then in vogue.

With the exception of Graham, it cannot be said that British or Irish chemists made any very remarkable contributions to science during the decade from 1830 to 1840. The number of workers was doubtless greater than at any previous period of the century. The volume of literature, as measured by the number of papers published, was more than double that of the first decade—one of the most momentous periods of our chemical history. But the efforts of workers at the time were spent more on

Berzelius	$\overset{\cdot\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{P}}+24\text{Aq.}$
"	$\overset{\cdot\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{P}}+24\overset{\cdot\cdot}{\text{H}}.$
Graham	$\overset{\cdot\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}.$
Rose	$\text{NaO}+\text{PO}^{\circ}+24\text{HO.}$
Whewell	$\text{N}+\overset{\cdot\cdot}{\text{p}}+24\text{q.}$
Brande	$\text{S}+\overset{\cdot\cdot}{\text{p}}+24\text{q.}$
Turner	$\overset{\cdot\cdot}{\text{S}}\text{o}+\text{P}+2\overset{\cdot\cdot}{\text{O}}+24\text{aq.}$
Johnstone	$\overset{\cdot\cdot}{\text{P}}+\overset{\cdot\cdot}{\text{S}}\text{O}+24\overset{\cdot\cdot}{\text{H}}.$
Prideaux	$\overset{\cdot\cdot}{\text{NP}}+24\text{Aq.}$
Warrington	$\overset{\cdot\cdot}{\text{Po}}+\overset{\cdot\cdot}{\text{So}}+24\overset{\cdot\cdot}{\text{H}}^{\circ}.$

points of detail, on the filling in of little gaps in the chemical structure, as it then existed, than in attempts at new developments.

Thomas Clark, mainly remembered for his method of determining the hardness of water, and for his discovery of pyrophosphoric acid, was studying the metallurgy of iron. Apjohn, whose name is best known in connection with his formula for determining the dew-point from the indications of the wet bulb hygrometer, contributed a few papers on mineral chemistry; Daubeny, a professor of chemistry to botanists, and a professor of botany to chemists, occupied himself principally with geological and botanical chemistry; Colonel Yorke studied the action of air and water on lead; Everitt investigated the behaviour of dilute sulphuric acid with potassium ferrocyanide, and discovered the salt which is associated with his name; Johnston made analyses of mineral substances of organic origin, investigated paracyanogen, certain cyanides, and double haloid salts; Kane analysed a few minerals and inorganic salts, the chlorides of iodine, and studied the action of ammonia on the chlorides and oxides of mercury, the composition of essential oils, and the nature of wood spirit. Penny made a remarkably accurate series of atomic weight determinations of chlorine, nitrogen, potassium, and sodium, which served still further to strengthen the case against the hypothesis that all equivalent numbers are simple multiples of that of hydrogen; and Gregory, the successor of Graham at the Andersonian College, a follower of Liebig, and one of the earliest chemists to introduce his methods into Britain, occupied himself with the study of pharmacological and organic products, the analysis of petroleum, and the destructive distillation of caoutchouc. Other chemical workers at this period were Pepys, Porrett, Edmund Davy, Brooke, Cooper, Daniel, John Mercer, William Herapath, Walter Crum, William West, Hennell, Scanlan, Teschemacher, Hugh L. Pattinson, Warrington, Andrews, Richardson, Robert D. Thomson, Denham Smith, Golding Bird, Solly, Fownes, Stenhouse, George Wilson, and Griffin.

But the general condition of scientific chemistry with us during this period was, no doubt, accurately characterised by Liebig, when he wrote to Berzelius in 1837:—"Ich bin einige Monate in England gewesen, habe ungeheuer viel gesehen und wenig gelernt. England ist nicht das Land der Wissenschaft, es existirt dorten nur ein weitgetriebener Dilettantismus, die Chemiker schämen sich Chemiker zu heissen, weil die Apotheker, welche verachtet sind, diesen Namen an sich gezogen haben. ... Graham macht auch in wissenschaftlicher Hinsicht die schätzbarste Ausnahme, er ist ein vortrefflicher Mensch, auch Gregory, der an seine Stelle in Glasgow gekommen ist."

It was at this low ebb in our fortunes that the Chemical Society was founded. It might seem, at first sight, an unpropitious time at which to launch a new Society for the purpose of publishing the work of chemical investi-

gators, when chemical investigation itself was so languidly pursued. But the seventy-seven gentlemen from all parts of the kingdom who enrolled themselves as the founders of the Chemical Society appeared to have had a robust faith in its ultimate success, and in the influence it was bound to exercise in stimulating chemical inquiry in these islands.

How far their faith was well founded—how far indeed this Society has succeeded in stimulating chemical research in this kingdom—I may possibly have an opportunity of showing on some future occasion. I hope also to be able to offer some account of the development of our means of teaching chemistry in this country during the century.

ON

BLACK PHOSPHORUS, AND THE CONVERSION OF PHOSPHORUS INTO ARSENIC.*

By T. FITTICA.

In a paper on "Black Phosphorus" F. A. Flückiger expressed his conviction that this so-called modification consists of nothing but arsenic, and he explains its occurrence in ordinary phosphorus, respectively, its apparent formation from phosphorus by means of ammonia, on the assumption that ordinary phosphorus contains an admixture of arsenic, the phosphorus dissolving in ammonia with the production of PH_3 , the arsenic remaining intact. My investigations, however, lead me to the conclusion that, by acting upon phosphorus with ammonia in the presence of air, a true transformation of phosphorus into arsenic takes place, and that the latter appears to be a nitrogen-oxygen compound of phosphorus.

In the first place, I confirmed the observation that, on treating ordinary phosphorus with concentrated (20 per cent) ammonia on the water-bath at about 60°C . (the phosphorus therefore in the fused state), with frequent shaking with free access of air, it is transformed into the black modification; that is to say, converted into arsenic. The operation is best carried out in a flask with a flat bottom and of considerably larger capacity than is necessary for the quantities of substances employed, in order that a large surface be presented to the air. The flask at the same time should carry a long glass tube, to prevent, as much as possible, the evaporation of the ammonia. The flask is from time to time removed from the water-bath for a short time and strongly shaken, in order to bring the fluid into contact with the air. The amounts of arsenic thus obtained are, however, but very small, and I therefore employed stronger oxidants than the oxygen of the air, taking hydrogen peroxide in the first instance.

When I warmed phosphorus with concentrated ammonia, and then added a recently prepared solution of hydrogen peroxide, allowing the mixture to stand at ordinary temperature for some length of time, I obtained somewhat larger quantities of arsenic. Even here, however, the amounts of arsenic produced were still very scant, and not sufficient for the confirmation of my suspicion that I had not to do with the detection of a contamination of phosphorus with arsenic, but with the real formation of the latter.

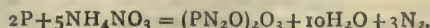
In order to obtain a secure basis for my conclusions I first resolved to examine the phosphorus, both ordinary colourless and amorphous red phosphorus, for its contents in arsenic. I found, however, that from equal amounts of phosphorus I obtained various quantities of arsenic, whether I used colourless or red phosphorus, or whether I used various oxidants. Generally the red phosphorus gave a larger proportion of arsenic by the usual oxidation with nitric acid, and especially when employing barium peroxide with hydrochloric acid or nitric acid, or potassium

chlorate and hydrochloric acid. The same sample of colourless phosphorus which with dilute nitric acid gave a hardly noticeable trace of arsenic, yielded with concentrated nitric acid very plainly discernible quantities of arsenic, and larger ones still with barium peroxide and nitric acid. (0.4274 grm. phosphorus yielded 0.0142 grm. arsenious sulphide, equal to 2.02 per cent As; 0.501 grm. phosphorus yielded 0.2012 grm. arsenic sulphide, equal to 2.5 per cent arsenic). [Note by Translator.—There is evidently an error in these figures]. From amorphous phosphorus upwards of 2.6 per cent arsenic can thus be obtained (1.3981 grms. yield 0.049 grm. As_2S_3 , equal to 2.13 per cent As; 0.2266 grm. gave 0.010 grm. As_2S_3 , equal to 2.64 per cent As).

Oxidation with barium peroxide and hydrochloric acid gave smaller yields, but I did not succeed in obtaining agreeing results on employing various quantities of the same substances. But when finally 1.02 grms. of the amorphous phosphorus was oxidised by carefully mixing it with barium peroxide, and heating the mixture with dilute sulphuric acid, or on adding to the mixture water and concentrated sulphuric acid (to 1 grm. P 13.63 grms. BaO_2 and 8 grms. H_2SO_4) a very small trace of precipitate obtained by sulphuretted hydrogen from the product of complete oxidation from which the barium sulphate had been filtered off, proved to be pure sulphur, completely soluble in CS_2 . The precipitate extracted with ammonia yielded a trace of substance which, however, was also completely soluble in CS_2 , and burned upon a platinum foil with a blue flame.

It was obvious therefore that the production of arsenic from the phosphorus employed was due to the nitric oxidants, and to the employment of ammonia, and I therefore tried to effect a synthesis of arsenic by using both nitric acid and ammonia together, and also by employing nitrites. If ordinary phosphorus is heated on the water-bath in a tube connected with a condenser, with ammonium nitrate, no reaction takes place below 60° , but the action then becomes so violent that explosions may take place, even in presence of ammonium carbonate, corresponding with the well-known fact that phosphorus burns in ammonium nitrate vapour, just as it does in a current of oxygen. When phosphorus is heated together with ammonium nitrate and potassium nitrite in presence of ammonium carbonate, an exceedingly violent reaction takes place at a temperature approaching 100° . Amorphous phosphorus, however, appeared more suitable for the synthesis, and after many fruitless experiments I ultimately arrived at the following process, which as far as I can at present say, gives a yield of from 8 to 10 per cent of the crude product:—

2 grms. amorphous phosphorus, free from arsenic as tested above, are carefully mixed with 12.9 grms of finely powdered ammonium nitrate, and the mixture is placed in a tube which must not be too narrow, and is heated on a sand-bath, the temperature slowly rising to 180° . A reaction ensues which must be moderated, if necessary, by removing the flame from the bath. The temperature is then gradually increased to 200° ; when the reaction is finished, the mass is allowed to cool, dissolved in water, the solution filtered and precipitated with sulphuretted hydrogen. The precipitate is dissolved in ammonium carbonate, and the arsenic sulphide precipitated from the solution can be identified by its behaviour with ammonia and hydrochloric acid, by its oxidation into arsenic acid, and precipitation with a magnesia solution, as well as by testing of the magnesia precipitate in a Marsh apparatus. In accordance with the decomposition of ammonium nitrate on heating, and with the above stated proportions of phosphorus and ammonium nitrate, the formation of arsenic from phosphorus appears to take place mainly in accordance with the following equation:—



But I have to remark, that besides this main reaction at least one secondary reaction takes place, as shown by the

* *Lepoldina*, Halle, vol. xxxvi., No. 3, March, 1900.

production of white fumes of neutral reaction. These fumes can be collected in water in which they dissolve. They contain phosphorus, and with sulphuretted hydrogen yield free sulphur. In accordance with the above equation arsenic would be a nitrogen-oxygen compound of phosphorus, corresponding to the formula PN_2O .

THE COMMERCIAL ANALYSIS OF COPPER.

By A. HOLLARD.

THE copper is separated and estimated by the electrolytic method. The impurities are separated in the following manners:—The antimony, nickel, cobalt, silver, and lead electrolytically; the arsenic by distillation; the sulphur and gold by precipitation; the iron is estimated volumetrically.

The apparatus used has already been described and illustrated (*Bull. Soc. Chim.*, Series 3, xxxiii., p. 291). According to the nature of the element to be deposited, the surface of the electrode must be polished or rough. Copper and lead (in the state of oxide) deposit best on a rough surface; antimony, nickel, and cobalt on a smooth surface; and silver on either.

Details of the Electrolysis.

Estimation of the Copper (Electrolysis in Acid Solution).—10 grms. of the granulated material are taken and freed from grease and particles of iron by means of ether and a magnet. The material is then placed in a 500 c.c. beaker, 6.5 c.m. diameter, and 18 c.m. high. To this are added 20 c.c. of sulphuric acid, and 30 c.c. of nitric acid, sufficiently diluted with water to prevent a too violent reaction. It is then covered with a funnel, stem downwards, and heated gently. With fine copper the solution is complete, but unrefined metal leaves an insoluble residue; in such a case the solution must be further heated to collect the precipitate, and to free it from copper salts. The solution is diluted to 200 c.c., and the electrodes, connected to the two poles of a battery, completely submerged in it. The beaker is covered with two half clock-glasses, and a current of 1 ampère passed through.

When the solution contains no more copper the beaker and the solution are removed, and the electrodes plunged rapidly into two glasses of distilled water; the one covered with copper is next plunged into strong alcohol, then still wet with alcohol, placed in an oven, and dried at 90° for about ten minutes, and weighed. The weight found, minus that of the electrode, is the weight of the copper, plus the silver deposited at the same time. The weight of the copper can thus be deduced when we know the weight of the silver which is determined later on. If the copper contains lead, only part of this latter will be deposited as oxide, the remainder keeping in solution. The precipitation of the copper under these conditions takes about twenty-four hours.

We must observe that the complete electrolysis of copper under the given conditions can only be effected with coppers very poor in arsenic and antimony. As a general rule the quantities of arsenic and antimony present are sufficiently high for them to be partially precipitated with the last traces of copper. In such cases the electrolysis is stopped when the blue colour begins to disappear, that is when less than 50 m.grms. of copper remain in the bath, and the copper which also contains the whole of the silver is weighed. The remainder of the copper is estimated, as described further on, after the separation of the arsenic and antimony, but whether all the copper has been removed or not, the analysis is continued as follows:—

Estimation of the Antimony (by Electrolysis in Cyanide Solution).—15 c.c. of hydrochloric acid is added to the solution, which is then evaporated to dryness. On cooling the residue is taken up with dilute hydrochloric acid,

heating to complete the solution. The solution, diluted to 100 c.c., is then saturated in the cold, with hydrochloric acid gas, and then heated with 200 c.c. of pure ordinary hydrochloric acid saturated with sulphuretted hydrogen. This precipitates nearly the whole of the arsenic, the copper and antimony remain in solution. After twelve hours it is filtered with a filter-pump through glass-wool covered with asbestos. The sulphide of arsenic thus separated is not kept, the estimation of the arsenic being made on another sample of the copper. 300 c.c. of pure water, and 300 c.c. of water saturated with sulphuretted hydrogen, are then added to the solution. The copper and antimony are thus completely precipitated. After standing for a few hours the sulphides of these two metals are filtered, washed with a solution of sulphydric acid, then dissolved in a mixture of cyanide of potassium at 20 per cent (62.5 c.c.), and concentrated sulphide of sodium (20 c.c.) (density 1.22, and prepared according to Classen). The solution thus obtained is diluted to 220 c.c. in a beaker 6 c.m. in diameter; the electrodes are completely immersed therein, and a current of 0.05 ampère passed for a whole night. The antimony is deposited integrally, and forms a very adherent steel-grey metallic layer. To obtain an adherent deposit the amount of antimony to be precipitated must not surpass 0.05 grm.

Precipitation of the Remainder of the Copper.—The copper remaining, with a few milligrams of arsenic, after the separation of the antimony, is precipitated electrolytically in the following manner:—Sulphuric acid is added until a precipitate is formed; it is then heated to drive off the sulphuretted hydrogen, and bromised hydrochloric acid added; this dissolves the precipitate. Evaporate to dryness, and take up with 10 c.c. of nitric acid and water; when the solution is effected, add 10 grms. of nitrate of ammonia, and dilute to 100 c.c. This solution is then electrolysed with a current of 1 ampère. For very small quantities of copper the colorimetric method may be used.

Estimation of Nickel and Cobalt (by Electrolysis in Solution of Double Ammoniacal Sulphate).—The liquid freed from copper by electrolysis, and from arsenic and antimony by sulphuretted hydrogen is heated to drive off the H_2S ; the iron is then peroxidised by adding nitric acid, and boiling the solution; the latter is then evaporated to dryness on a sand-bath until white sulphuric fumes appear. The residue is taken up with dilute sulphuric acid, and then with water to dissolve everything. It is then treated with ammonia, and more sulphuric acid if necessary, so that each 100 c.c. of solution will contain 8 to 11 c.c. of ammonia combined with sulphuric acid. A slight excess of ammonia is then added to precipitate the iron; after boiling, the solution is allowed to cool, and 12 to 20 c.c. more of ammonia at 10 per cent is added per 100 c.c. of solution. Dilute to 250 c.c., and allow the peroxide of iron to collect at the bottom of the beaker. The electrodes are completely immersed in the clear liquid, and a current of 0.5 ampère passed. After a night the nickel and cobalt are completely precipitated. Wash and dry the electrode A as described for copper, then weigh. If the proportions of nickel and cobalt are wanted separately, they can be estimated by any known method. The maximum quantity of metal to have an adherent deposit is 0.2 grm.

Volumetric Estimation of the Iron.—The peroxide of iron is thrown on a filter, then dissolved in the smallest possible quantity of hydrochloric acid, and estimated by Mohr's iodine method.

Estimation of the Lead (by Electrolysis in Acid Solution).—A fresh sample of 10 grms. of copper is attacked by dilute nitric acid containing 50 c.c. of acid at 36° B. The liquid, filtered if necessary, and diluted to 350 c.c., is submitted to electrolysis; the intensity of the current should be 0.3 ampère. After eighteen hours the lead is precipitated integrally on the positive electrode A in the state of oxide in a very adherent deposit, brown or black according to the thickness, while the copper is partially deposited on the negative electrode B. The electrode A is then

plunged successively into two vessels filled with distilled water, then placed in an oven which is gradually heated to 200°. Under these conditions the oxide of lead corresponds exactly to the formula PbO_2 ; it is sufficient to multiply its weight by 0.866 to get the corresponding weight of metallic lead.

Estimation of the Silver (by Electrolysis in a Cyanide Solution, and Volumetrically).—If the copper is rich in silver, the copper deposited electrolytically on the electrode A is dissolved in nitric acid of 1.2 density; we know it must contain all the silver. In the opposite case we dissolve a fresh sample of 10 to 50 grms. of copper, according to the supposed amount of silver present; boil to drive off the nitrous fumes, filter if necessary, and precipitate the solution at 70° with a few drops of hydrochloric acid; this temperature is maintained until the precipitate collects. Filter, wash with warm water, and re-dissolve the precipitate in cyanide of potassium, and dilute to 250 c.c.; the solution should contain 2 per cent of cyanide of potassium. The current should be 0.05 ampère. After one night the precipitation is complete. This precipitate might be weighed, but it is better to dissolve it in nitric acid diluted with its own volume of water, and titrate by Volhard's sulphocyanide method. But in order that the precision of this method may be greater than that by weighing, the end of the reaction must be determined, not as Volhard says, by the appearance of the red colouration due to ferric sulphocyanide, but by titrating back by means of titrated nitrate of silver from this red colouration to the white appearance of sulphocyanide of silver. The distinctness of this latter reaction is incomparably greater.

The silver is therefore dissolved in about 100 c.c. of a mixture of equal volumes of nitric acid and water, and heated to boiling to drive off all nitrous fumes. The cooled solution is treated with 5 c.c. of ammoniacal iron alum at 20 per cent then with a titrated solution of sulphocyanide of ammonium until the red colour appears. A titrated solution of nitrate of silver (2 grms. of silver per litre) is then added until the red colour passes to pink, and then becomes suddenly white. The titrated solutions of sulphocyanide of ammonium and of nitrate of silver must correspond exactly, so that it will suffice to subtract from the number of c.c. of sulphocyanide used the number of c.c. of nitrate of silver added, and multiply this difference by 2 to obtain the weight of the silver in milligrams.

Estimation of the Arsenic (by Distillation and Volumetrically).—In a flask of 300 c.c. capacity we place 5 grms. of the granulated metal with 50 grms. of ferric sulphate.* Then, through a funnel provided with a stop-cock, we add 150 c.c. of pure hydrochloric acid; the flask is connected with a U-tube immersed in an oil-bath, and thence through a bent tube the gases pass into a test-jar. After pouring the acid into the flask the tap is closed, and after seeing that the oil-bath is at 150° to 175° the flask is gently heated. The metal dissolves, and the arsenic distils as arsenious chloride; this chloride is collected in the test-jar containing 50 c.c. of water. The operation is stopped in about half an hour, when 35 c.c. of the chloride has passed over. Under these conditions the arsenic alone passes into the test-jar, the antimony remaining in the flask, and in the U-tube which contains glass beads: this tube further retains all the projections which might be carried over from the flask. The arsenious solution obtained by distillation is titrated by iodine as follows:—Ammonia is added to the cooled solution until alkaline, it is then re-acidulated by a few drops of hydrochloric acid, and a slight excess of bicarbonate of soda added. The solution is then cooled again, 5 c.c. of 1 per cent starch added, and titrated with iodine until the blue colour is persistent. The titrated solutions are prepared in the following manner:—

Arsenious Acid.—Weigh out 3.3 grms. of pure arsenious acid (= 2.5 grms. arsenic) in fine powder, and 9 grms. of bicarbonate of soda. Treat the mixture with 500 c.c. of boiling water, and prolong the boiling until all the arsenious acid is dissolved. Cool, add 2 grms. of bicarbonate of soda, and make up to 1 litre, 1 c.c. = 0.0025 gm. of arsenic.

Solution of Iodine.—Dissolve 3.3 grms. of pure iodine in 50 c.c. of a 20 per cent solution of iodide of potassium, dilute to 1 litre, and titrate with 20 c.c. of the arsenious acid solution; 1 c.c. of the solution of iodine should correspond with 0.001 gm. of arsenic. Care must be taken to make all the estimations on the same volume of liquid, and to observe the number of tenths of a c.c. necessary to obtain a permanent blue colour in a solution free from arsenic. The titration of the solution of iodine should be repeated occasionally.

Solution of Starch.—Boil 10 grms. of potato starch in a litre of water. Add 1 gm. of potash alum as an anti-septic, and after cooling, decant the clear liquid. This solution will keep for several months.

Estimation of the Gold (in the Metallic State).—100 grms. of copper are dissolved in 750 c.c. of nitric acid of 1.2 density, boil to drive off the nitrous fumes, and filter. The filter which contains all the gold is dried, and then burnt. The residue is cupelled with lead and a little silver. The silver button, obtained by cupellation, containing all the gold is dissolved in nitric acid of 1.2 density, the gold which remains undissolved is dried and weighed.

Details of the Operation.—The filter with its contents are placed on a small sheet of thin, pure, lead about 7 cm. square, weighing about 20 grms. The paper is set fire to, and left to burn alone; after the combustion a few centigrams. of silver are placed on the lead, and the whole wrapped up tightly, and placed on a cupel in a red-hot muffle. After cupellation the flattened button is placed in a matras with nitric acid (free from chlorine), of 1.2 density; the slightly inclined matras is heated gently until all nitrous fumes are driven off. The clear liquid is then decanted with great care, and the matras partially filled with pure water and again decanted. If necessary the washing may be repeated; finally, the matras, filled with water, is inverted into a small clay crucible; when the gold has fallen into the crucible the matras is removed, the water in the crucible is poured off, and the crucible dried in front of the muffle; when dry it is placed in the muffle, and heated strongly for a few minutes. On cooling, the gold, which should be of a yellow colour, is placed on the balance and weighed.

Estimation of the Sulphur (in the State of Sulphate of Barium).—From 5 to 20 grms. of copper, according to its richness, are attacked with aqua regia, with an excess of nitric acid, and the sulphur in the solution is estimated by the known method.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 8.

Estimation of Acetic Acid in Commercial Acetates, and its Separation from Propionic, Butyric, and Formic Acids.—R. Haberland.—The four acids are set free by means of phosphoric acid, and distilled in a current of steam. The distillate is treated with PbO and evaporated; the residue is taken up with water, and the basic propionate of lead is left in the insoluble state. The filtrate is freed from lead by sulphuric acid, treated with ZnO , and evaporated to dryness. The residue is taken up with alcohol, which will not dissolve the acetate or butyrate. The alcoholic solution is evaporated to dryness, the mass treated with phosphoric acid, and the acids distilled; they are then transformed into silver salts, the salt of butyric acid being very slightly soluble in water.—*Zeit. Anal. Chem.*, xxxviii., p. 217.

* This sulphate must be freed from all trace of nitrous fumes by evaporation in the presence of an excess of sulphuric acid, after having been finely powdered.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 17th, 1900.

Professor THORPE, F.R.S., President, in the Chair.

MESSRS. John R. Brooke, J. Wallace Sandford, and Bertram D. Steele were formally admitted Fellows of the Society.

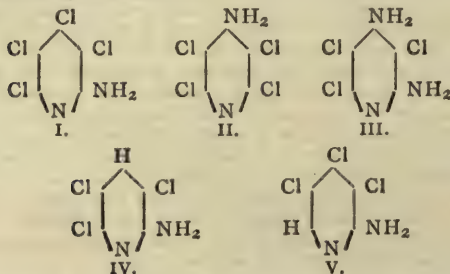
Certificates were read for the first time in favour of Messrs. Charles Berjew Brooke, Colne House, near Manningtree, Essex; Ernest Owen Courtman, Denford House, Atkin's Road, Clapham Park, S.W.; Henry Bertie Gritton, The Cottage, Balmain, Sydney, N.S.W., Australia; John Beresford Leathes, 10, Park Mansions, Battersea Park, S.W.; Sidney Scrivener Napper, 144, Highbury New Park, N.; Oswald Silberrad, Sunny Croft, Buckhurst Hill, Essex; John Traquair, Glenfield Starch Works, Paisley.

The following Certificates were approved by Council under Bye-law I. (3):—Angelo Cantin, Vacas, Mauritius; M. C. Nanjunda Row, Mylapore, Madras; M. Goolab Roy, Chintadrepettah, Madras.

Of the following papers, those marked * were read:—

*67. "The Chlorine Derivatives of Pyridine. VI. The Constitution of some Aminochloropyridines." By W. J. SELL, M.A., and F. W. DOOTSON, M.A.

The authors gave an account of their work on the constitution of various aminotrichloro- and aminotetrachloropyridines which have recently been described by them. The two compounds which result from the action of ammonia on pentachloropyridine (*Trans.*, 1898, lxxiii., 777), and which melt at 174–175° and at 212–213°, are shown to have the constitutions represented by the formulæ I. and II. respectively.



Both compounds heated with ammonia to a higher temperature give the same diaminotrichloropyridine, which must therefore be represented by formula III.

To the aminotrichloropyridine, obtained by the action of ammonia on tetrachloroisonicotinic acid (*Trans.*, 1897, lxxi., 1083), the constitution represented by formula IV. was provisionally assigned (*Trans.*, 1899, lxxv., 980). This has now been completely established.

The aminotrichloropyridine, obtained (*Trans.*, 1899, lxxv., 980) by the action of sodium carbonate on a compound containing two pyridine rings, was shown to have the constitution represented by formula V.

*68. "Ortho-substituted Nitrogen Chlorides and Bromides, and the Entrance of Halogen into the Ortho-position in the Transformation of Nitrogen Chlorides." By F. D. CHATAWAY and K. J. P. ORTON.

When phenylacetyl nitrogen chloride undergoes transformation, a mixture of *o*- and *p*-chloroacetanilide is produced in the proportion of 95–96 per cent of the latter together with 4–5 per cent of the former.

The following compounds were described:—

Orthochlorophenylacetyl nitrogen chloride (acetyl chloro-amino-2-chlorobenzene), $C_6H_4Cl \cdot NCl \cdot COCH_3$, colourless, long, flattened prisms, m. p. 88°.

Orthobromophenylacetyl nitrogen bromide (acetyl bromo-amino-2-bromobenzene), $C_6H_3Br \cdot NBr \cdot COCH_3$, yellow, four-sided prisms, m. p. 150–152°.

Both of these compounds undergo transformation into the 2:4-disubstituted acetanilides.

DISCUSSION.

Dr. HEWITT pointed out that Beilstein and Kurbitow (*Annalen*, 1875, clxxvi., 36) had separated the ortho- from the para-chloraniline by distilling the mixed sulphates with steam, this method being employed by them on account of the difficulty of isolating pure *o*-chloronitrobenzene from the mixture obtained on nitrating chlorobenzene.

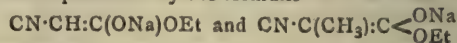
Dr. COLLIE pointed out that if a compound were obtained in which the halogen was attached to a nitrogen atom which was not directly united to the benzene nucleus, it was possible that isomeric change involving the production of a meta-substitution product might result.

*69. "Ammonium Imidosulphite." By EDWARD DIVERS and MASATAKA OGAWA.

The authors have discovered a compound, $3NH_3 \cdot 2SO_2$, which has the constitution $HN(SO_2NH_2)_2$ and bears the same relation to the amidosulphite as that which exists between imidosulphate and amidosulphate. When ammonium amidosulphite is allowed to decompose completely in a current of well dried hydrogen or nitrogen at a temperature not exceeding 35°, it leaves a coloured residue which is practically insoluble in absolute alcohol. This residue, freely soluble in water, can (with the exception of a small quantity of sulphate) be dissolved by repeated treatments with alcohol of 90 per cent. Rejecting the coloured fractions first obtained, the remainder of the solution on evaporation over sulphuric acid deposits bright micaceous crystals of the new salt ammonium imidosulphite. The mother liquor, which contains much ammonium amidosulphate, must be removed by careful washing with 95 per cent alcohol. The imidosulphite is very deliquescent, and all samples so far prepared have an acid reaction towards litmus, due to the loss of a little ammonia. By dissolving the ammonium salt in 75 per cent alcohol and adding exactly the equivalent quantity of alcoholic potash, the pure crystalline potassium imidosulphite, slightly alkaline to litmus, is obtained. The imidosulphites react with silver nitrate similarly to the amidosulphites, and give with barium chloride a precipitate which readily dissolves in acids, forming a solution which acquires the odour of sulphur dioxide, and deposits barium sulphate.

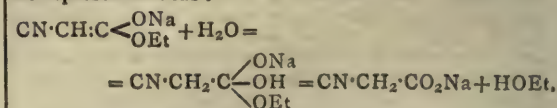
*70. "The Constitution of Ethyl Sodiocyanacetate and of Ethyl Methylsodiocyanacetate." By JOCELYN FIELD THORPE.

The author pointed out that the reactions of ethyl sodiocyanacetate and of ethyl methylsodiocyanacetate are best represented by the formulæ—



respectively.

When ethyl sodiocyanacetate is dissolved in water, the solution is not alkaline, and on evaporation in a vacuum leaves sodium cyanacetate. The changes involved may be represented thus:—



The production of acid ethyl salts frequently observed in the condensation of ethyl cyanacetate with unsaturated ethyl salts can be thus explained, as the sodium compound of the condensation product, on treatment with water, would yield in a similar way the corresponding sodium ethyl salt. The acid ethyl salts on distillation lose carbon dioxide, and pass into the corresponding nitriles.

A number of such condensations were described, and the conditions given under which the maximum quantity of acid ethyl salt is produced. Experiments were described showing that prolonging the time of heating increases the quantity of neutral ethyl salt at the expense of the acid ethyl salt. This is explained by assuming that the first step is the addition of a molecule of alcohol to the unsaturated sodium compound.

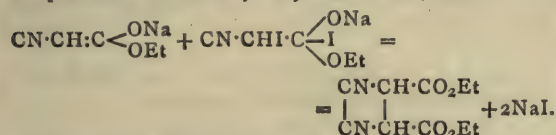
Ethyl methylsodiocyanacetate behaves in the same way as ethyl sodiocyanacetate, but its solubility and deliquescent nature render its purification difficult. It condenses with unsaturated ethyl salts to form acid ethyl salts, the yields of which, however, were never more than 17 per cent of those theoretically possible.

The equation $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et} + \text{CH}_2\cdot\text{C}(\text{CH}_3)\cdot\text{CO}_2\text{Et} = \text{CN}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CN}(\text{CH}_3)\text{CO}_2\text{Et}$, usually supposed to represent a reaction of this kind, is shown to be wrong, because on treating the product of the reaction with methyl iodide, the ethyl salt obtained gives on hydrolysis the symmetrical *aa'*-dimethylglutaric acids, and not the unsymmetrical *aa*-dimethylglutaric acid.

Small quantities of *cis*- and *trans*-acids such as are obtained from ethyl cyanacetate and ethyl methylcyanacetate, may be separated by the following method:—The cyanoethyl salt is converted by treatment with methyl alcoholic potash into the cyano-acid, which is then boiled with concentrated hydrochloric acid as long as carbon dioxide is evolved. The *cis*- and *trans*-amides, the intermediate products formed, are finally converted, the former into the imide, the latter into the *trans*-acid. The imide is insoluble in dilute sodium carbonate solution, and can thus be separated from the *trans*-acid.

*71. "The *aa*₁*ββ*-Tetramethylglutaric Acids." By JOCELYN FIELD THORPE and W. J. YOUNG.

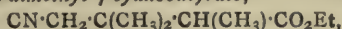
Ethyl Sodiocyanacetate, $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{ONa})\text{OEt}$, separates from absolute alcohol in lustrous plates; with water it gives (see preceding abstract) sodium cyanacetate; with an ice cold solution of iodine in ether, it reacts to form *ethyl iodocyanacetate*, $\text{CN}\cdot\text{CHI}\cdot\text{CO}_2\text{Et}$, a brown oil which decomposes on distillation under diminished pressure; an intermediate addition compound is, however, formed, which reacts with unchanged sodiocyanacetate at higher temperatures to form *ethyl dicyanosuccinate*, thus:—



Ethyl dicyanosuccinate separates from dilute alcohol in glistening plates which melt at 120°.

With bromine dissolved in carbon bisulphide, only *ethyl bromocyanacetate*, $\text{CN}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$, was obtained as a brownish oil which decomposes on distillation under diminished pressure.

Ethyl methylsodiocyanacetate, $\text{CN}\cdot\text{C}(\text{CH}_3)\cdot\text{C}(\text{ONa})\text{OEt}$, is not precipitated on the addition of alcoholic sodium ethoxide to ethyl methylcyanacetate, but is obtained as a gelatinous precipitate on adding an equal volume of dry ether to the solution. It combines with iodine to form *ethyl methyliodocyanacetate*, $\text{CN}\cdot\text{C}(\text{CH}_3)\cdot\text{I}\cdot\text{CO}_2\text{Et}$, a brown oil decomposing on distillation under diminished pressure. It condenses with ethyl dimethylacrylate to give the acid salt, $\text{CO}_2\text{H}\cdot\text{CH}(\text{CN})\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{Et}$, which, on distillation, loses carbon dioxide and gives *ethyl a-methyl-ββ*-dimethyl-γ-cyanobutyrate,—



a fairly mobile oil boiling at 224°, which, on hydrolysis, gives *αββ*-trimethylglutaric acid melting at 87°. The preparation of *ethyl a-cyano-ααββ*-tetramethyl glutarate, b. p. 174–176°, and its conversion into *tetramethyl glutarimide* (m. p. 108°), and into *trans-αββα'*-tetramethyl glutaric acid (m. p. 98°) are described. The imide is converted by

heating for two hours with 50 per cent sulphuric acid into the *cis*-acid which melts at 140°, and this, on treatment with acetyl chloride, yields its anhydride, a liquid boiling at 155–160° (30 m.m.). The *cis*-acid is partially converted into the *trans*-acid by heating it in a sealed tube with concentrated hydrochloric acid.

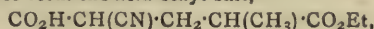
*72. "β-Isopropylglutaric Acid, and the *cis*- and *trans*-Methyl Isopropyl Glutaric Acids." By F. H. HOWLES, J. F. THORPE, and W. UDALL.

The main facts regarding β-isopropylglutaric acid have already been described (*Proc.*, 1899, xv., 103).

By the action of methyl iodide on the sodium compound of the product resulting from the condensation of ethyl sodiocyanacetate with ethyl β-isopropylacrylate, *ethyl a-cyano a-methyl-β-isopropyl glutarate* is obtained as a thick oil boiling at 180–183° (25 m.m.). This on hydrolysis with methyl alcoholic potash yields the corresponding potassium salt, from the acidified aqueous solution of which the solid cyano-acid may be obtained; this, on boiling with concentrated hydrochloric acid, passes into a mixture of the imide and the *trans*-acid. *a-Methyl-β-isopropyl glutarimide* separates from water in colourless needles melting at 114–115°. *Trans-a-methyl-β-isopropyl glutaric acid* separates from water in microscopic crystals melting at 102°, and is converted into the anhydride of the *cis*-modification on heating with acetic anhydride in a sealed tube.

The *cis*-modification (obtained from the imide by heating with 50 per cent sulphuric acid) crystallises from water in glistening plates melting at 137°, and on treatment with acetic anhydride is converted into the anhydride which crystallises from light petroleum in prisms melting at 44°.

Ethyl sodiocyanacetate condenses with ethyl *a-methyl acrylate* to form the acid ethyl salt,—



which on distillation yields *ethyl a-methyl-γ-cyanobutyrate*, a mobile oil boiling at 205°, giving on hydrolysis *a-methylglutaric acid*.

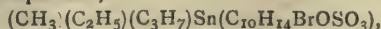
By a similar method to that above described *ethyl a-cyano-αα'-dimethylglutarate* (b. p. 181–183°), the potassium salt of the cyano-acid, the *cyano-acid* and the *cis*- and *trans-αα'-dimethylglutaric acids* were prepared.

Ethyl-β methyl-γ cyanobutyrate and *β-methylglutaric acid* have also been obtained in a similar manner.

*73. "The Racemisation of Optically Active Tin Compounds. Dextromethylethylpropyl Tin Dextrobromocamphorsulphonate." By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

The authors have shown (*Proc.*, 1900, xvi., 42) that the aqueous solution obtained by treating externally compensated methylethyl-*n*-propyl tin iodide with aqueous silver dextrocaphorsulphonate yields only dextromethylethylpropyl tin dextrocaphorsulphonate on evaporation to dryness. They attributed this behaviour to progressive racemisation of the levorotatory radicle, $(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)\text{Sn}$, attending crystallisation of the sparingly soluble salt of the dextrorotatory radicle. As this, the first well-determined case of the kind recorded, has an important bearing upon the space configuration of quadrivalent sulphur compounds (*Proc.*, 1900, xvi., 12), and upon the preparation of compounds owing their optical activity to the asymmetric nitrogen atom (*Trans.*, 1899, lxxv., 1127), it seemed to merit further investigation.

On treating externally compensated methylethyl-*n*-propyl tin iodide with silver dextro-*a*-bromocaphorsulphonate in warm aqueous solution and evaporating the filtered liquid, *dextromethylethylpropyl tin dextrobromocamphorsulphonate*,—



separates in colourless plates which, after crystallisation from acetone, melt at 194–197° with previous softening; the mother-liquors yield, on evaporation, further deposits of the same salt, and no trace of salt of the levorotatory base could be obtained. The behaviour of the dextro-

camphorsulphonate and the dextrobromocamphorsulphonate is thus the same, the whole of the laevorotatory base, $(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)\text{Sn}\cdot\text{OH}$, becoming converted into its dextrorotatory isomeride. In dilute aqueous solution, the bromocamphorsulphonate has the molecular rotation $+318^\circ$, which, accepting Walden's value $[\text{M}]_{\text{D}} = +270^\circ$, for the bromocamphorsulphonic acid radicle, allows $[\text{M}]_{\text{D}} = +48^\circ$ for the basic radicle; the value, $[\text{M}]_{\text{D}} = +45^\circ$, previously obtained from the dextrobromocamphorsulphonate is thus confirmed.

A crucial test of the truth of the explanation based on progressive racemisation is now possible, for if the intramolecular mobility of the base, $(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)\text{SnOH}$, is such that racemisation can effect total conversion of the externally compensated base into the dextrorotatory component, the reverse should occur under favourable conditions. A 1 per cent aqueous solution of the crystalline dextrobromocamphorsulphonate was made in the cold, and the molecular rotation of the dissolved salt was found to be $+318^\circ$. The solution was then sealed up in a tube and heated on the water-bath for two hours; after cooling, the molecular rotation was found to be now only $+273^\circ$. As the molecular rotation of the acid is $+270^\circ$, the base must exist wholly racemised in the solution. Some of the solution was then evaporated to dryness on the water-bath, and, after cooling, made up to its original volume by dissolving the residue in cold water; the molecular rotation of the salt in this solution had risen to $+315^\circ$. This experiment was repeated with similar results. Further, the addition of potassium iodide solution to aqueous solutions of dextromethylethylpropyl tin dextrobromocamphorsulphonate before and after heating on the water-bath caused the deposition of dextrorotatory and of optically inactive methylethylpropyl tin iodide respectively.

These facts afford the complete proof that on evaporating externally compensated methylethylpropyl tin hydroxide with either of the optically active acids, the laevo-base is wholly converted into the dextrocomponent by progressive racemisation.

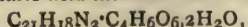
DISCUSSION.

Prof. PERCY FRANKLAND called attention to the remarkable mobility of the groups attached to the atom of tin which was quite without parallel in the case of groups attached to carbon. In no asymmetric carbon compound with which he was acquainted had anything comparable to this facility of racemisation been observed.

74. "Racemic and Optically Active forms of Isoamarine." By H. LLOYD SNAPE, D.Sc., Ph.D.

The author has examined the behaviour of the isoamarine previously described by Brooke and himself (*Trans.*, 1899, lxxv., 208) towards nitrous acid, alkyl iodides, acetyl chloride, and nitric acid. Each of these agents acts upon ordinary amarine: and it was desired to contrast the products obtained from the two bases. But, although isoamarine entered readily into reaction in every case, the products were so unstable that as yet the author has failed to prepare them in pure condition.

As the result of further investigation, the anticipation of Japp and Moir (*Trans.*, 1900, lxxvii., 613), that isoamarine is the racemic form of amarine was fully confirmed. Isoamarine, itself optically inactive, was resolved by means of tartaric acid into the acid tartrates,—



of the *d*- and *l*-bases, the salt of the *d*-base being much less soluble than that of the *l*-isomeride. From the respective tartrates, the corresponding bases were obtained by precipitation with ammonia. The *l*-base was more difficult to obtain in a state of purity; but it was evident that the optical antipodes had been obtained, the one giving for $[\alpha]_{\text{D}} +62.02^\circ$, and the other -61.30° to -58.65° , these values being determined in ethyl acetate solution, after the rotation had become constant.

The racemic base has a higher melting point and

density, but a smaller solubility, than the optical antipodes.

Mr. W. J. POPE has kindly measured the crystals of *d*- and *l*-isoamarine, and states that they are orthorhombic prisms, sphenoidally hemihedral, the crystals of the *d*-base showing the form $O - k\{111\}$, whilst those of the *l*-iso-

meride show the form $O + k\{111\}$. The crystals of the two substances are thus enantiomorphously related.

The racemic base was synthesised from the *d*- and *l*-isomerides by mixing them in alcoholic solution; but neither of the latter was racemised when heated alone with alcohol to 200° .

PHYSICAL SOCIETY.

Ordinary Meeting, May 25th, 1900.

Prof. J. D. EVERETT, F.R.S., Vice-President, in the Chair.

PROF. S. P. THOMPSON showed some Experiments Illustrating the Aberration called Coma.

If a converging lens is placed obliquely in a parallel beam of light, instead of giving a point image, it produces unilateral distortion, and the bright central spot is accompanied by a pear-shaped tail which is known as a coma. The direction in which this tail points depends upon the side of the lens which is presented to the light. With a concavo-convex lens, the convex surface gives an inward pointing coma, and the concave surface an outward pointing coma. The existence of this phenomenon is due to unequal magnification from different zones of the lens—a fact which was shown by covering the lens with a zone plate of three or four rings, and viewing on a screen the distorted images of the several zones. The form of a coma varies greatly with the distance of the screen from the lens. A parallel beam of light which has passed obliquely through a convex lens, is capable of producing some curious shadows. The shadow of a rod can be obtained as a circular spot, and that of a grating, made by stretching threads between two rods, as concentric circular rings. Prof. Thompson also showed a stringed model illustrating the paths of light rays in the formation of a coma.

Mr. R. T. GLAZEBROOK then read some "Notes on the Measurement of some Standard Resistances."

Three methods have been employed by the author for building up multiples of a standard resistance, such as a 1-ohm coil. The first method consists in making as accurately as possible three 3-ohm coils. These in parallel can be compared directly with the standard by Carey Foster's method. Their resistance in series is very approximately nine times that in parallel, and hence an accurate determination of a resistance about 9 ohms can be obtained. If, then, this resistance is put in series with the standard an accurately known 10-ohm resistance is obtained. By a similar process, a hundred or a thousand ohm coil can be built up. The second method consists in calibrating a resistance box. The 1-ohm coils of the box are compared directly with the standard and the other resistances determined accurately by a building-up process, using a subsidiary resistance box. In comparing the high resistances, the difference between the two boxes may be so great as to send the balance off the bridge-wire. In these cases the third method is employed. The equal arms of the bridge are accurately known, and one of them is shunted with a resistance, which need not be accurately known, until the reading is brought back on to the wire. The coils chiefly used throughout the experiments were made of platinum silver.

Mr. CAMPBELL asked if the same degree of accuracy could be obtained with manganin coils; if so, then the small temperature change of manganin would be an advantage.

Mr. TROTTER asked if proper allowance could be made for the large number of mercury cups used in Method 1.

Mr. RENNIE advocated the use of the build-up box in preference to the first method. With two mercury cups there is less chance of errors escaping notice than with eight. Every 10 or 100 ohm coil tested at the Board of Trade is subjected to a comparison with a box calibrated by a build-up process.

Dr. HARKER asked if the resistance of the eight mercury cups in series had ever been measured, and, if so, what was the magnitude of the result and what the uncertainty?

Mr. GLAZEBROOK said he had investigated the resistance of the mercury contacts, and it was negligible. In answer to Mr. Campbell, the author said he had no experience of manganin coils himself, but he had seen some figures for German coils which agreed very closely.

Mr. J. J. GUEST then read a paper "On the Strength of Ductile Materials under Combined Stresses."

The author throughout his experiments has used the "yield-point" of a material as the true criterion of its strength, and has rejected the elastic limit as being modified by local yielding. At present two theories are used in the calculation of strengths of materials. The first is that the material yields when one of the principal stresses reaches a certain amount. This theory, which was adopted by Rankine, and is used by engineers in England and America, is not in accord with recent experiments. The second theory is that the material yields when the greatest strain reaches a certain amount. This was advocated by St. Venant, and is used by engineers on the Continent. Besides these, there is a third theory of elastic strength, in which the condition of yielding is the existence of a shearing stress of a specific amount. In the case of a solid bar subjected to torsion, there is a variation in the strain from the axis outwards, and consequently the materials have been used in the form of thin tubes. This allows the application of an internal fluid pressure. The specimens were of steel, copper, and brass; the state of set caused by drawing having been removed by annealing. The tubes were subjected to—(1) torque, (2) torque and tension, (3) tension only, (4) tension and internal pressure, (5) torsion and internal pressure, and (6) internal pressure only. The axial elongation, the twist, and occasionally the circumferential strain, were measured. Towards the end of the experiments observations were made on bending; the results disprove the maximum stress theory, and are at variance with the maximum strain theory. The maximum shearing stress developed, and the corresponding shearing strain, were comparatively constant throughout the experiments, and no other simple relation between the stresses or strains was even approximately constant. The results of the experiments have been plotted synoptically on a curve, and the several lines have been drawn upon which these points should lie according to the various theories. It is readily seen that the points cluster round the line which represents the existence of a specific shearing stress; the author therefore favours the existence of this stress for any material.

The CHAIRMAN read a communication upon the subject from Dr. CHREE. Mr. Guest, in his paper, has regarded the shearing stress theory as a little known one. As the shearing stress is half the difference between the greatest and least principal stresses, this theory is the same as Prof. G. H. Darwin's maximum stress-difference theory. All the theories suppose that the stress-strain law is linear, and that strains are so small that their squares and products can be neglected. Mr. Guest concludes that, in ordinary materials, the law is linear to the elastic limit, which answers to a stress lower than that which answers to the yield-point, and that yield-point phenomena arise between these. Nevertheless, he focusses attention on the yield point as the criterion of strength, and assumes that Hooke's law holds up to it,

Prof. PERRY congratulated the author upon his paper, and said there was no time left to discuss it at length. The results obtained gave information upon a subject of which very little is known experimentally.

The Society then adjourned until June 8th.

CORRESPONDENCE.

DISTILLATION WITHOUT BUMPING.

To the Editor of the Chemical News.

SIR,—On p. 678 of "Select Methods in Chemical Analysis" some suggestions are given to avoid bumping in distilling certain fluids. Having occasion to prepare some absolutely pure sulphuric acid (Fresenius's "Qualitative Analysis," §24 A), I introduced (what first came to hand) a few small fragments of ordinary tobacco pipe, and the effect was surprising: the acid distilled away quite calmly, the fluid being covered with bubbles, and the acid dropping regularly into the receiver. I rested the retort ($\frac{1}{2}$ litre) upon 1 square inch of asbestos felt resting on a thick clay crucible lid over a large sized Bunsen flame.

I send you this in case you should think the suggestion worthy of mention in the CHEMICAL NEWS, as it may not have been remarked before.—I am, &c.,

G. F. M. FIELDING, M.A.,

Asst. Curate of Staplehurst.

Staplehurst, R.S.O.,
May 24, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 19, May 7, 1900.

Preparation of β -Alcoyloxy- α -Cyanocrotonic Ethers,

$\text{CH}_3\text{—COR}=\text{C} \begin{smallmatrix} \text{CN} \\ \text{CO}_2\text{C}_2\text{H}_5 \end{smallmatrix}$, Isomers of the Acetoalcoylcyanacetic Ethers, $\text{CH}_3\text{CO}=\text{C} \begin{smallmatrix} \text{CN} \\ \text{R} \end{smallmatrix} \text{—CO}_2\text{C}_2\text{H}_5$.

—A. Haller.—The silver derivative of acetylcyanoacetic ether, when acted upon by alcoholic iodides, causes the formation of those particular ethers whose properties correspond exactly to those of bodies containing an enolic ether function, and not to those whose molecules contain the methinic cetonic function, as the class of acetocyanacetic ethers would lead one to suppose. The presence in these latter of two negative radicles, $\text{CN}.\text{CO}_2.\text{C}_2\text{H}_5$, allows of the tautomerism of the molecule, and of changing the cetonic group into an enolic group with the conditions under which the author worked. The results of the experiments lead naturally to the question as to whether acetocyanacetic ether and its analogues really

exist in the free state under the form $\text{R}.\text{CO}.\text{CH}.\text{CO}_2.\text{C}_2\text{H}_5$, justified by their synthesis, or whether, however prepared, they do not allow of a molecular transposition which makes the β -oxy- α -cyanocrotonic ethers. This property can only be solved by physical methods which the author proposes to investigate.

Heat of Neutralisation of Hydrogen Peroxide by Lime.—M. de Forcrand.—The author continues his research on the subject of the action of oxides on peroxide of hydrogen by substituting lime for the baryta used in his former experiments. The lime, when used in dilute solution, forms with hydrogen peroxide two successive

compounds, the one very rich in oxygen, which has not been isolated, an unstable peroxide or perhaps a compound, $\text{CaO}_2 + 9\text{H}_2\text{O}_2$; the other, which may be either $\text{CaO} \cdot 2\text{H}_2\text{O}_2$ or $\text{CaO}_2 \cdot \text{H}_2\text{O}_2$, or possibly $\text{CaO}_3 \cdot n\text{H}_2\text{O}$. This latter is analogous to the known compound $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$. Calorimetric numbers are given for the various proportions used of CaO and H_2O_2 .

Solubility of a Mixture of Salts having a Common Ion.—Charles Touren.—The author performs his experiments under the same conditions as those used for his preceding research on the nitrate and chloride and the nitrate and bromide of potassium. He finds (1) the solubility of potassium chloride in solution of the bromide increasing in concentration, and (2) the solubility of the solid bromide in solutions of the chloride. The study of the solubility of a mixture of salts allows of the recognition of isomorphous salts, when direct proofs are difficult to find.

Action of Phenyl Isocyanate and Aniline on some γ -Cetonic Acids.—T. Klobb.—The author draws the following conclusions from the investigation:—(1) The so-called γ -cetonic acids are transformed under the influence of phenylisocyanate into acid anhydrides, anilides, and pyrrolones. (2) When the acid anhydride is an olide, it does not finally react on the carbanilide, as the acyclic anhydrides studied by M. Haller, it is necessary therefore to substitute aniline. (3) When acids contain two non-substituted groups, CH_2 , there are usually formed coloured polymers of pyrrolones, or, more exactly, bodies which are derived by the subtraction of two molecules of water from two molecules of anilide.

New Halogen Mercuric Derivatives of Antipyrine.—J. Ville and Ch. Astre.—In a preceding paper, the authors described a new chlor-mercuric compound of antipyrine corresponding to the formula $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_2\text{HgCl}_2 \cdot \text{HCl}$. Under analogous experimental conditions, they have obtained the corresponding bromine and iodine compounds.

Acetyl-phenyl Acetylene and Benzoyl-phenyl Acetylene.—Ch. Moureu and R. Delange.—Under the influence of boiling alkalis, acetyl-phenyl acetylene, a ketone with acetylenic function, $\text{C}_6\text{H}_5\text{—C}\equiv\text{C—CO—CH}_3$, becomes split up into acetic acid, $\text{CH}_3\text{—CO}_2\text{H}$, and phenyl-acetylene, $\text{C}_6\text{H}_5\text{—C}\equiv\text{CH}$; whilst benzoyl-phenyl acetylene, another acetylenic ketone, $\text{C}_6\text{H}_5\text{—C}\equiv\text{C—CO—C}_6\text{H}_5$, becomes split up into benzoic acid, $\text{C}_6\text{H}_5\text{—CO}_2\text{H}$, and acetophenone, $\text{C}_6\text{H}_5\text{—CO—CH}_3$.

Stability of Solutions of Saccharose.—Echsner de Coninck.—The author finds that an aqueous solution of saccharose, carefully kept from solar light and the action of mould, at ordinary temperatures is relatively very stable, even in the presence of slight oxidising influences. As soon as moulds begin to form, two sets of transformations take place—first inversion, and then fermentation—producing carbonic acid gas and ethylic alcohol.

Study of the Hydrolysis of Fibrous Tissue.—A. Etard.—The hydrolysis by sulphuric acid of the fibrous tissue of beef causes the formation of a polysaccharide, but does not show any notable quantity of leucine. Glycoprotein is not generally formed, $\text{C}_n\text{H}_{2n+1}\cdot\text{NO}_2 + \text{C}_n\text{H}_{2n-1}\cdot\text{NO}_2 = \text{C}_n\text{H}_{2n}\cdot\text{N}_2\text{O}_4$. All the oxygen is not evolved in the form of carbonyl; a part of the tissues from which it is derived are formed into amino-saccharides.

MISCELLANEOUS.

Research on the Ortho-plumbates of the Alkaline Earths.—G. Kassner.—The author first establishes the fact that the meta-plumbate of calcium, obtained by him by heating the crystalline ortho-plumbate, $\text{Ca}_2\text{PbO}_4 \cdot 4\text{H}_2\text{O}$, and by Grützner and Höhnelt by treating Ca_2PbO_4 with Na_2O_2 , or the ortho-plumbate with a solution of KOH ,

contains $4\text{H}_2\text{O}$, answers to the formula $\text{CaPbO}_3 + 4\text{H}_2\text{O}$, and only loses three-quarters of its water at 300° . When heated in a current of pure air it gives a more oxygenated plumbic compound. This new compound is a true peroxide having an acid character; this would be perplumbic acid, of which the anhydride should be Pb_2O_5 ; as this latter is the true peroxide the compound PbO_2 should be called peroxide no longer, but binoxide.—*Archiv der Pharm.*, 237, p. 409.

Purification of Acetylene.—M. Pfeiffer.—At the acetylene works which supplies this gas to the Hungarian State Railways chloride of lime was formerly employed as the purifying material. They now use a mixture of chloride of lime and plumbate of soda containing an excess of alkali. Chloride of lime alone is likely to cause the explosion of the acetylene on account of the liberation of chlorine. A purifier charged with the new mixture was opened after ten hours working. When the upper grating, covered with lime, was removed, spontaneous combustion took place, and a long flame rose from the apparatus, but there was no explosion. Under the above conditions therefore we may say that the new mixture is not dangerous.—*Journ. f. Gasbeleucht.*, lxii., p. 551.

MEETINGS FOR THE WEEK.

TUESDAY, 5th.—Royal Institution, 3. "Ruskin, the Servant of Art," by R. Warwick Bond, M.A.

THURSDAY, 7th.—Royal Institution, 3. "Chaucer," by the Rev.

Canon Ainger, M.A., LL.D.

Chemical, 8. "Diphenyl- and Dialkyl-ethylene-

diamines—their Nitro-derivatives, Nitrates, and

Mercuriochlorides," by W. S. Mills, M.A.

"Condensation of Ethyl Acetylenedicarboxylate

with Bases and β -Ketonic Esters," by S. Ruhe-

mann, Ph.D., and H. E. Stapleton, B.A. "The

Constitution of Pilocarpine," by H. A. D. Jowett,

D.Sc. "The Nitrogen Chlorides derivable from

m-Chloroacetanilide, and their Transforma-

tions," by F. D. Chattaway, D.Sc., K. J. P.

Orton, Ph.D., and W. H. Hurlley. "Deriva-

tives of Cyanocamphor and Homocamphoronic

Acid," by A. Lapworth, D.Sc.

FRIDAY, 8th.—Royal Institution, 9. "The Effect of Physical Agents

on Bacterial Life," by Allan Macfadyen, M.D., &c.

Physical, 5. "On the Magnetic Properties of Iron

and Aluminium Alloys" (Part II.), by Dr. S. W.

Richardson. "Note on Crystallisation produced

in Solid Metal by Pressure," by W. Campbell.

"On the Viscosity of Mixtures of Liquids and of

Solutions," by Dr. C. H. Lees.

SATURDAY, 9th.—Royal Institution, 3. "The Growth of Chamber

Music" (with Musical Illustrations), by Sir

Frederick Bridge, Mus. Doc.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2175.

RADIO-ACTIVITY OF URANIUM.*

By Sir WILLIAM CROOKES, F.R.S.

(Concluded from p. 255).

18. In making photographic tests it is not necessary to take much of the substance. On an ordinary microscopic slide I put a small drop of liquid from each of the highest five fractionations, Nos. 10, 9, 8, 7, and 6. The drops were allowed to crystallise and the slide was laid on a sensitive plate. In twenty-four hours a good impression of No. 10, the highest fraction, was obtained; a less strong impression of the next, No. 9; a fainter one of 8; a scarcely perceptible one of 7; and no impression at all from No. 6. The slide containing the five crystalline spots was then covered with another glass, and the whole cemented together with Canada balsam and mounted in the manner usual with microscopic slides. When the balsam was dry the slide was put on a sensitive plate. In twenty-four hours a good graduated image was developed.

19. There are in commerce two kinds of uranium nitrate: one, the commercial variety, and another called "purissimum." I am informed that the "purissimum" is prepared from the former by repeated crystallisation. I purchased some of each of these nitrates and tested them on a photographic plate. The commercial variety proved to be at least twice as radio-active as the "purissimum" salt.

20. Experiments were now instituted with a view of obtaining a wholly inactive uranium nitrate. About two pounds of the salt that had been obtained from the solution in ether was repeatedly crystallised, pouring off the mother-liquor each time. This and the next succeeding two lots of crystals (Nos. 1, 2, and 3) were put into cells, and kept on a sensitive plate for seven days. On developing the plate no image could be detected where No. 1 had been; a scarcely perceptible impression could be just detected at No. 2, and a little stronger impression at No. 3.

21. Other methods were attempted for the separation of the active substance from uranium. Uranium nitrate fuses at a moderate temperature, and after some time it becomes darker, and nitrous fumes come off. Finally, the mass becomes semi-fluid, and will not run. The operation is then stopped, and the mass transferred to water; the undecomposed nitrate is dissolved out, leaving an insoluble basic nitrate. The basic nitrate is of an orange-yellow colour, easily dissolved in nitric acid to again form the normal nitrate. By using this method of fractionation the active body gradually accumulates towards the basic end, but the method is neither so complete nor so easily effected as the crystallisation method, and therefore I have not pushed it very far. I have, however, proved that the radio-activity of nitrate of uranium can be concentrated by fractionation to the basic nitrate end, the nitrate at the other end being diminished in radio-activity.

22. A highly active uranium nitrate, prepared by fractionation from the part insoluble in ether, was dissolved in water, and ammonia in excess was added. Yellow ammonium uranate was precipitated. The filtrate was evaporated to dryness, and heated with nitric acid. The yellow precipitate and the residue of the filtrate were put into cells, and laid on a sensitive plate. After twenty-four hours' action the plate was developed, when it was seen that the whole of the radio-activity resided in the

ammonium uranate, the other substance showing nothing. This experiment proves that the active body is precipitated by ammonia, and is insoluble in excess.

23. Another portion of active uranium nitrate was dissolved in water, with an excess of ammonium carbonate. The first-formed precipitate almost entirely re-dissolved, leaving a small quantity of insoluble light brown flocculent precipitate. This collected on warming, like alumina. It was filtered off, well washed and dried, and put in a glass cell.

The filtrate from the above precipitate was evaporated to drive off the ammonium carbonate, when a yellow precipitate came down. This was filtered, washed, dried, and put into a cell.

These precipitates were exposed for twenty-four hours in a lead screen apparatus. On developing, it was seen that the residue insoluble in ammonium carbonate instantly flashed out black and dense, while the salt precipitated from the ammonium carbonate solution gave a scarcely discernible image.

24. The action of the precipitate insoluble in ammonium carbonate was so strong that another experiment was tried, exposing the sensitive plate to its action for one hour. On development, the disc of action came out strong and black, although not so black as in the twenty-four hours' experiment. It was now laid for five minutes on a sensitive plate. Here the action was distinct—about as strong as that given by ordinary uranium nitrate in twenty-four hours. These experiments prove that the active body can exist apart from uranium.

If a sheet of thin glass or celluloid is laid on a sensitive plate, and the dried filter-paper with its contents laid on that, and kept down by a weight, an impression is given in as short a space of time as if a glass cell had been used.

25. The radio-active body is not entirely insoluble in ammonium carbonate. A portion of the very active precipitate left after separation from the uranium was dissolved in dilute hydrochloric acid, and an excess of ammonium carbonate added. The precipitate was very brown, due to the presence of iron; it was dried and tested. The filtrate was well boiled, and as the ammonium carbonate evaporated a slight precipitate came down. This was collected on a filter and tested by the side of the first precipitate. On developing the plate the images produced by each precipitate were of about equal intensity. The brown precipitate was digested in very dilute hydrochloric acid in the cold. The iron partially dissolved before the rest of the substance, leaving the residue decidedly paler in colour. This pale body was just as radio-active as before the partial removal of the iron. Therefore the presence of iron does not interfere with the activity of the substance.

26. Having thus definitely proved that the supposed radio-activity of uranium and its salts is not an inherent property of the element, but is due to the presence of a foreign body,* it is necessary patiently to determine the nature of the foreign body. Several radio-active bodies claimed to be new have already been extracted from pitchblende, and experiments have been instituted to see if the newly found body Ux had similar chemical properties to those of the older active substances.

27. Polonium was first tried. A photographic plate had a thin sheet of celluloid laid on it, and over this a sheet of aluminium foil, 0.05 m.m. thick. On this double layer were put two cells, one containing basic polonium nitrate, the other active Ux . Action was allowed to proceed for twenty-four hours, and the plate was then developed. A disc of blackening was seen under where the Ux stood, the action having passed through the glass, celluloid, and aluminium. Under the polonium nitrate no trace of action could be detected.

The experiment was repeated, minus the aluminium foil, and the action continued only two and a quarter

* For the sake of lucidity the new body must have a name. Until it is more tractable I will call it provisionally Ux —the unknown substance in uranium.

* A Paper read before the Royal Society, May 10, 1900.

hours. On development, the UrX was found to have acted well, while the polonium showed no trace of action.

28. This behaviour of polonium being eccentric or contrary to published accounts,* I put some polonium nitrate in a very thin gelatin capsule, and laid it for eight hours on a sensitive plate. No trace of an image could be seen on development.

The same polonium nitrate was put in a watch-glass, and the sensitive plate put *over it* face downwards, so that it might be exposed to the direct emanations from the polonium nitrate. On the top of the plate was laid a sheet of lead to press it tight to the edges of the watch-glass.

The exposure was continued for twenty-eight hours. On developing, a strong action was seen, strongest in the middle where opposed to the thickest part of the heap of polonium nitrate, and weaker towards the edge. A well-marked action took place all over the plate exposed to the interior of the watch-glass, but it was sharply cut off at the edges. This confirms the previous results—that the emanations from polonium are of a different character to those from radium or UrX, both of which pass through glass, aluminium, and lead.

29. Another property of polonium sharply distinguishing it from UrX is volatility. The discoverers first obtained it by subliming pitchblende *in vacuo*. Afterwards they used this property to separate it from bismuth, the polonium and the bismuth sulphides depositing at different parts of the hot tube.

A strongly radio-active compound of UrX was ignited in a blowpipe flame with the addition of a drop of sulphuric acid. Its radio-activity, on a sensitive plate, was not diminished by this treatment. This experiment was tried several times at increasingly higher temperatures, and always with the same result.

30. Polonium is precipitated by sulphuretted hydrogen, in an acid solution. An acid or neutral solution of UrX is not precipitated by this reagent. Therefore I am justified in saying my UrX is not polonium.

31. But it is not so easy to settle whether UrX is distinct from radium, although many arguments point to its not being radium. The discoverers of radium give several of its chemical properties, and in most of these UrX and Ra are entirely different. Thus, radium sulphate is said to be insoluble in water and acids, while UrX dissolves easily to a clear solution in dilute sulphuric acid. Radium salts are said to be not precipitated by ammonium sulphide or by ammonia, while UrX is precipitated by both.

32. It was hoped that doubtful points might be settled conclusively by the spectrum, as both radium and polonium give well-defined and characteristic lines, especially in the ultra-violet part of the spectrum where I have chiefly worked. M. Demarçay (*Comptes Rendus*, vol. cxxiv., p. 716; *CHEM. NEWS*, vol. lxxx., p. 259) has given a list of some of the principal lines in the radium spectrum between the wave lengths 3649.6 to 4826.3, the one at 3814.7 being very strong, and those at 4683.0, 4340.6, and 3649.6 being next in intensity. He draws special attention to the line at 3814.7 as the line showing first in a compound poor in radium. In none of my UrX compounds have I been able to detect a trace of this line; on the other hand

I have failed to photograph this line in products which I know contain radium. The reason is my radium compound is too weak. M. Demarçay says the line is scarcely visible with a radium compound only sixty times as active as uranium. My substance containing radium was still weaker, judging from its action on a photographic plate.

33. The same reasoning applies to polonium. With polonium I have obtained strong lines in the ultra-violet, but I can detect none of them in the spectrum of my compound of UrX. All that I can see are lines belonging to—

Platinum (from the poles),
Uranium,
Calcium,
Aluminum,

and a few of the strongest air-lines, besides a large number of faint lines difficult to identify.

34. Spectrum experiments having failed to show a difference between radium and UrX, it was thought that possibly some information might be gained by submitting them to the radiant matter test, which has proved so fruitful in its application to the yttrium earths. Some of the most active UrX was put in a tube furnished with a pair of terminals, and it was exhausted to a high point, heat being applied during exhaustion. Simultaneously a self-luminous radium compound was sealed in a vacuum tube and exhausted, heat being likewise applied. When fully exhausted a strong induction spark was passed through each tube. The UrX compound phosphoresced of a fine blue colour. In the spectroscopic no discontinuity could be seen in the spectrum of the phosphorescent light.

Under the influence of the induction spark, the radium compound phosphoresced of a luminous rose-colour, showing in the spectroscopic a concentration of light in the red-orange, and a very faint citron band, due to a trace of yttrium, probably an impurity.

35. A powerful radium compound and one of UrX, each in a glass cell, and a paper tray full of polonium subnitrate, were placed side by side, and a strip of white card was put as a reflector at the back. In front a photographic camera was arranged so as to throw full-sized images of the polonium, UrX, and radium compounds on a sensitive plate, and the whole was kept in total darkness for five days. On development, the image of the radium with the containing bottle was visible, but not a trace of image from the polonium could be seen. This confirms previous observations that the radiations from polonium will not pass through glass. Those from radium and UrX easily penetrate glass and other media (28).

36. Recently claims have been put forward for the existence of a third radio-active body in pitchblende. In the *Comptes Rendus* for October 16, 1899, and April 2, 1900, M. A. Debierne describes a radio-active body, to which he gives the name of "Actinium." At first he said "actinium" showed the principal analytical properties of titanium, but later he describes it as not resembling titanium in all its reactions. M. Debierne gives many reactions of the new substance, and in some instances they are like those of radium. But he qualifies them by the statement that they cannot yet be considered as belonging definitely to the new radio-active substance, because up to the present it has not been obtained sufficiently concentrated. He believes rather that these reactions should be looked upon as the result of retention, analogous to that of iron oxide by barium sulphate. He says that the chemical reactions of the most active substance which he obtained, together with its spectroscopic examination, showed that it chiefly consists of thorium. He cannot, however, be sure that it resembles thorium in all its reactions.

37. Experiments have been commenced to see if it is possible to separate thorium compounds into an active and an inactive body. A strong solution of thorium

* "The rays emitted by compounds of polonium render barium platino-cyanide fluorescent. . . . To make the experiment, place on the active substance a very thin sheet of aluminium, and on this a thin layer of barium platino-cyanide; in the dark the barium platino-cyanide appears feebly luminous over the active substance" (M. and Mme. Curie and M. Bémont, *Comptes Rendus*, vol. cxxvii., p. 1215; *CHEM. NEWS*, vol. lxxix., p. 1). "Polonic rays act on sensitive plates. The substance we call sulphide of polonium gives a good impression after only three minutes, and there is a decided action noticed after even half a minute" (Mme. Curie, *Revue Générale des Sci.*, January 30, 1899; *CHEM. NEWS*, vol. lxxix., p. 77). In the same paper the authoress, after describing the power possessed by a polonium compound to excite phosphorescence, says, "the rays emitted by this latter body have traversed the aluminium and excited the fluorescence of the platino-cyanide above it." It is evident from the above extracts that I was justified in thinking that polonium rays were not entirely stopped by thin aluminium, glass, or celluloid.

sulphate was slightly acidulated with sulphuric acid, and gradually raised to the boiling point. A copious precipitate of sulphate came down, and was filtered hot. The precipitate was dissolved in cold water, and the solution re-heated, when a precipitation of the sulphate again occurred. The mother-liquor from one crystallisation was added to the crystals from another in the systematic manner adopted in fractionation, and when the operations had proceeded some time a test was made on the "head" and "tail." A small quantity of solution from each was evaporated to dryness and strongly ignited before the blowpipe. The two lots of earth were put in cells and a sensitive plate exposed to their action for seventy-two hours. On development not the slightest difference could be detected between the impressions produced by either of the fractions.

I next tried partial crystallisation of thorium nitrate, fractionating it in the way already described in the case of uranium (15). Great difficulties were here encountered, owing to the tendency of a strong solution of thorium nitrate to remain supersaturated for several days, when it would suddenly crystallise to a solid mass. After some weeks, however, six fractionations were effected, and tests were made on the first and last of the series.

The sensitive plate was exposed to their action for 120 hours. On development, the fraction at the first end (crystals) gave a very feeble action, while that at the other end (mother-liquor) gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance.

By the kindness of Dr. Knöfler, of Berlin, who makes thorium nitrate by the ton, I have at my disposal some specially prepared thorium nitrate, which is chemically pure. Thoria prepared from this, tested on a sensitive plate, gave a feeble impression in 120 hours.

38. In the present state of our knowledge of these radio-active bodies it is safest to retain an open, or even a slightly sceptical mind. We recognise them mainly by the photographic and the electrical tests—reactions which are so sensitive that they give strong results, even when the active body is present in too small a quantity to be detected by its spectrum—one of the most delicate of tests. Knowing the tendency of ordinary chemical bodies to be carried down when a precipitate is formed in their presence, even when no question of sparse solubility is involved, it is not surprising that radium and actinium, to say nothing of Ux , appear to simulate elements which may ultimately prove to be very different from them in chemical characters. For instance, Ux dissolves easily in dilute sulphuric acid, and, I have reason to believe, forms a soluble sulphate; still, when chloride of barium is mixed with it and precipitated as a sulphate, I invariably find strong radio-activity in the precipitated sulphate as well as in the filtrate from the barium sulphate.

To adduce a simile from my previous researches, the first surmises as to the chemical characteristics of the bodies now known to be yttrium and samarium, were widely different from reality. The differences were entirely due to the perturbing cause which is active in the present case—the tendency of the bodies to be carried down and entangled in precipitates, where, according to ordinary chemical laws, they ought not to occur; and to the extreme delicacy of the radiant matter test, which in the case of samarium detects one part in $2\frac{1}{2}$ million parts of calcium, and in the case of yttrium detects one part in the presence of a million parts of extraneous matter.

39. The radiographic test for these active bodies presents another point to be borne in mind. Other tests for the presence of an element either act quickly, or do not act at all, with a comparatively narrow margin of debateable land where the indications of the test may be doubtful. Here, however, the test is cumulative. Like an astronomer photographing stars too faint for his telescope to disclose, he has only to expose the plate for a sufficiently long time and the star reveals itself on development. So, in the case of radio-active minerals or precipitates,

if no action is apparent at the end of an hour, one may be shown after twenty-four hours. If a day's exposure will still show nothing, try a week's. Considering my most active Ux does not contain sufficient of the real material to show in the spectrograph, yet is powerful enough to give a good impression on a photographic plate in five minutes, what must be its dilution in compounds which require an hour, a day, or a week to give an action?

ON THE PHOTOGRAPHY OF THE SMALLEST WAVE-LENGTHS OF LIGHT RAYS.*

By VICTOR SCHUMANN, Leipzig.

My observation of the spectrum beyond the wave-length $185\ \mu$ —which work I have resumed after several years' interruption—led to the following results:—

1. The photographic examination of this region of the spectrum now succeeds in much less time than formerly, in consequence of repeated improvement of my means of observation. The hydrogen lines at $100\ \mu$ require as the result only a few seconds' exposure.

2. The transparency of quartz diminishes appreciably with the wave-length. A plate of quartz of $0.5\ \text{m.m.}$ thickness absorbs nearly all rays beyond $150\ \mu$.

3. White fluor-spar behaves similarly, but up to $100\ \mu$ is much more transparent than quartz, but it weakens in a striking degree all the more refrangible rays. For example, in only $0.5\ \text{m.m.}$ thickness, it more than doubles the time of exposure. This loss of light depends less on the thickness of the fluor-spar than on the number of its reflecting surfaces which the rays pass through.

4. Hydrogen in this region possesses a second line spectrum; it appears at atmospheric pressure, and only with the spectrum caused by discharge between the electrodes. It strongly resembles the low pressure spectrum, but shows also rays of other wave-lengths and a somewhat different distribution of energy. The production of the metallic spectra is complicated by the simultaneous appearance of the lines of this spectrum, so that the ascertainment of the origin of individual lines still presents difficulties.

5. Metallic spectra require much longer illumination than the low pressure spectrum of hydrogen. Firstly, because the metallic spark produced in an atmosphere of hydrogen acts materially weaker than in air; and, secondly, because—from above-mentioned reasons—a considerable portion of the active light is lost in the fluor-spar window separating the discharge area from the vacuum spectrograph.

THE TRANSPARENCY OF THIN FILMS OF GLYCERIN.

By Dr. VICTOR SCHUMANN.

THE use of glycerin for joining together the halves of the Cornu quartz prisms induced me to determine the absorption relations of this medium, especially towards the most refrangible aluminium rays. The result thus obtained, in consideration of the frequent use of these prisms in spectrum photography, is so far important that glycerin is not so indifferent towards the above-mentioned regions of the spectrum as it has proved to be in the less refrangible ultra-violet, according to the observations of Eder and Valenta.

* Read before the Imperial Academy of Sciences in Vienna, March 29th, 1900.

According to my experience, two quartz plates, cut perpendicularly to the axis, containing a glycerin film 0·1 m.m. thick, increased the times of exposure of the aluminium rays—

No. 30, λ 199 μ , from 18·0 to 25·0

No. 31, λ 194 μ , from 11·4 to 25·0

No. 32, λ 185 μ , from 0·08 to 25·0

When I afterwards stuck the two quartz plates together with a very small quantity of glycerin, to prevent reflection at the two inside surfaces and to obtain the thinnest film possible, the times of exposure on repetition of the experiment were considerably less increased, viz. :—

No. 30 and No. 31, from 19·5 to 25·0

No. 32, from 17·5 to 25·0

These numbers prove how much the transparency of a double quartz prism depends on the thickness of its glycerin film, and that the unobstructed passage of the most refrangible rays is only possible with an extremely thin layer of glycerin. That this combining medium should be preferred in certain circumstances to the dry contact of the prism halves (provided that the glycerin film is not much thicker than in the last-mentioned case) can be concluded from the values obtained when the quartz plates are laid dry upon one another. The dry plates lengthened the time of exposure of the rays—

No. 30 and No. 31, from 16·8 to 25·0

No. 32, from 15·0 to 25·0

From all these values, it is evident that the most refrangible rays must be carefully dealt with in order to obtain their intensity undiminished.

With regard to the less refrangible ultra-violet downwards to wave-length 227 μ , I may mention that I was not able to detect with certainty any influence of the glycerin film 0·1 m.m. thick. It is possible that a want of sensitiveness in my instruments, not specially adapted to photometric work, is responsible for this negative result. But it must not be said that the absorption vessel with its contents did not affect the photographic action. On the contrary, it lengthened—in consequence of loss of light resulting from reflection—the time of exposure for the region from 361 μ to 227 μ almost uniformly from 21·5 to 25·0. As for the more refracted rays, which gave evidence of the influence of the glycerin, the time of exposure—for example, at Cd No. 25, λ 220 μ , and at Cd No. 26, λ 215 μ —rose from 19·5 to 25·0, whilst under otherwise similar conditions the glycerin vessel alone caused a rise from 21·5 to 25·0 only.

NOTE ON THE PECULIAR DIFFICULTIES WHICH BESET THE APPLICATION OF THE AMMONIA METHOD TO THE ANALYSIS OF SEWAGE AND SEWAGE EFFLUENTS.

By J. ALFRED WANKLYN.

In our treatise on "Sewage Analysis," published this day (May 12th), last year, my colleague, Cooper, and myself, remarked as follows :—

"The ascertainment of the true figure for the albumenoid ammonia in sewage and sewage effluents involves some practical difficulties, and we fear that much of the work put forward by our chemical brethren is invalid. We suspect that serious errors, both in the direction of an over-estimate and an under-estimate, have been made on many occasions when sanitary officials have employed the ammonia method in the examination of sewages and sewage effluents."

Within the last few months I have had very striking evidence of the necessity of the warning which I have just quoted.

The following is a characteristic example of the serious

analytical divergencies which occur when the ammonia method is applied to very similar and presumably identical sewage effluents by two independent analysts.

Results obtained by analyst A. :—

Sewage effluent No. 1 gave 1·00 albumenoid ammonia.

"	"	No. 2	"	0·80	"	"
"	"	No. 3	"	1·10	"	"
"	"	No. 4	"	0·80	"	"
"	"	No. 5	"	0·80	"	"
"	"	No. 6	"	0·90	"	"
"	"	No. 7	"	0·90	"	"
"	"	No. 8	"	0·90	"	"
"	"	No. 9	"	0·80	"	"

Results obtained by analyst B. :—

Sewage effluent No. 1 gave 3·80 albumenoid ammonia.

"	"	No. 2	"	6·85	"	"
"	"	No. 3	"	13·50	"	"
"	"	No. 4	"	8·00	"	"
"	"	No. 5	"	8·50	"	"

The practical effect of the two series of analyses being that, whereas the analyses by analyst A. showed that the effluent was very good, the analyses by analyst B. showed that the effluent was utterly bad.

The two sorts of effluents were not of quite the same date, but they were effluents from the same sewage works.

If not quite identical in composition, they were doubtless very similar in character and composition; and, if correctly carried out, the analysis of the two sets of effluents would, I believe, have exhibited that similarity.

I am personally acquainted with analyst A., and know that he adopted special precautions to avoid the mistake of returning ammonia which had been derived from urea as if it had been derived from substances coming under the category of the albumenoid group of substances.

With analyst B. I have no personal acquaintance whatever. Apparently the gentleman is personally known to, and enjoys the confidence of, one of the lecturers on Public Health, whose knowledge of the analysis of sewage by the ammonia method appears to have been derived from my treatise on "Water Analysis" before the publication of the "Sewage Analysis" last year.

In reference to the description of the analysis of sewage given in my treatise on "Water Analysis," I have to say that that description was, of course, only supplementary to the main subject of that book, and that it was very much abridged, and, unless read with more intelligence and care and discrimination than might fairly be demanded, it might have led the analyst into error.

One of the greatest difficulties of sewage analysis—perhaps I should say the chief difficulty of sewage analysis—depends upon the extraordinary properties of urea.

Urea is very prone to undergo transformation into carbonate of ammonia by reaction on some of the water in which it is dissolved.

In many sewages, the great bulk of the urea originally present in the urine has undergone this change before the sewage leaves the sewers. But there are great differences in this respect in different sewages. Sometimes fully half of the original urea remains undecomposed in the sewage as it leaves the sewer. In such cases an analyst working the ammonia method in a somewhat perfunctory manner—laboriously, but not discreetly—and without the special information to be found in our recent book on sewage-analysis, might be expected to obtain results similar to those found by analyst B. The following experiments, recently made in my laboratory, are instructive and much to the point :—

Fresh urine, sp. gr. 1018·4, was mixed with good London water from the Lambeth Water Company in the proportion of one volume of urine to 99 volumes of water. A considerable quantity of this dilute solution of urine was prepared for the purpose of experiment.

The same day, whilst it was fresh, this dilute urine was

submitted to analysis in the "somewhat perfunctory manner—laboriously, but not discreetly"—and without regard to the special information contained in the treatise on "Sewage Analysis." It yielded:—

	Milligrams. per litre.
Free ammonia	12.50
Albumenoid ammonia	49.00

In this case the dilute urine, representing sewage or sewage effluent, was almost quite unfermented, and the old and well-known but seldom worked method of chemical transformation of the unfermented urea into carbonate of ammonia was not resorted to. The correct figure for the albumenoid ammonia instead of being 49.00 milligrams. per litre was only about 6.00 when the method was properly worked.

After keeping the dilute urine for ten days at the ordinary temperature of the atmosphere, it was again analysed, and gave totally different results, owing to the circumstance that after that length of time the fermentation of the urea into carbonate of ammonia had run its course. The results were as follows:—

	Milligrams. per litre.
Free ammonia	100.00
Albumenoid ammonia	3.50

The point to which I desire to direct attention is that no return of the albumenoid ammonia in sewage or sewage effluent is trustworthy unless adequate precautions have been taken to avoid mistaking urea for the complex nitrogenous organic substances which yield albumenoid ammonia.

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THE ESTIMATION OF MOLYBDENUM IN STEEL AND STEEL-MAKING ALLOYS.

By FRED IBBOTSON and HARRY BREARLEY.

It is no easy matter to arrive at a satisfactory conclusion from published opinions as to the influence which the presence of molybdenum exerts on steel. Von Lipin (*Stahl und Eisen*, xvii., 571), points out that such steels need very careful heat treatment during the working of them; that after hammering at a heat not exceeding a cherry-red, they are quite clean and free from the small cracks which are often present in tungsten steels; that compared with a steel containing an equal amount of tungsten, one containing molybdenum is softer, that is, gives greater elongation; that the results of water hardening are more, and of oil hardening less marked; and that molybdenum steel will bear more mechanical punishment without developing cracks. Experiments at the Creusot Works showed that in the presence of chromium even a few tenths per cent of molybdenum were advantageous in the manufacture of armour plates. Amongst other particular properties of molybdenum Moissan and others have pointed out that it would prove valuable as a deoxidising agent in the converter and elsewhere during the manufacture of steel, as the MoO_3 produced would be quite volatilised.

Mo has been found in the specular iron ore of Sweden by Ingelström, in Belgian coal by Armand Jorissen, in pig-iron by Ledebur, and in blast-furnace refuse by several observers. If we remember that tungsten compounds are rarely free from molybdenum, and that tungsten steel is an important commercial product, it is very likely that molybdenum has been frequently overlooked, particularly as its analytical characters so much resemble those of tungsten.

At present, steel which actually contains notable quantities of Mo is rare; many analysts have never had a sample passed through their hands. A lamentable il-

lustration of this statment is the fact that small amounts of Mo in cast-iron have been mistaken by two English chemists for a new element.

This comparative rarity is doubtless accountable for the fact that no English text-book, so far as we know, devoted to metallurgical analysis, gives instructions for estimating Mo in iron compounds. Carnot has, so we are informed, described a process in the *Annales des Mines*, which we have, however, not seen.

In our earliest experiments we obtained satisfactory results by fusing the oxidised alloy with Na_2CO_3 , extracting with water, reducing the filtrate with zinc, and titrating with permanganate. This process was used by Benneville (*Journ. Iron and Steel Inst.*, 1895, i., 202).

In this and a subsequent paper we offer gravimetric methods for the estimation of Mo and W, which are based on the various processes elaborated in our recent papers on the analysis of Mo and W compounds.

Molybdenum in Steel.—It has been shown already (*CHEM. NEWS*, lxxix., 3), that the separation of Fe and Mo increases in accuracy as ammonium acetate, hydrate, sodium carbonate, or sodium hydrate are used, and that with the last reagent in particular absolute accuracy of separation may be obtained when the iron present is only two or three times greater than the Mo. In preparing a series of test analyses to illustrate the value of the method for both high and low percentages, it became very plain that from about 15 per cent of Mo downwards, the separation was inaccurate.

The strong likeness between the behaviour of chromic and molybdic acids in relation to their separation from iron has already been commented on. Still it is important here to re-emphasise the fact that on adding an alkali to an acidified mixture of ferric chloride and molybdic acid, a point is reached at which insoluble basic ferric molybdate is formed, and that no perfect separation of the two metals is possible until sufficient alkali has been added to decompose this compound. For the separation of small amounts of iron this excess need not be a large one, so long as the precipitant be of the right kind; but as the amounts of iron in association with molybdic acid become larger and larger, the same excess of the precipitant becomes less and less able to effect a complete separation. The addition of increasing amounts of soda hydrate improves the separation only very slowly after a certain approximate separation is reached, and no system of aerating the precipitated flocks of ferric hydrate, such as by the use of a mixture of sodium hydrate and carbonate, will effect the desired end.

A description of an entirely satisfactory process applied to a steel or ferro molybdenum of small Mo content is as follows:—

Dissolve a suitable amount (say 2 grms.), of the sample in HCl. The unusual character of the metal is at once indicated by the colour of the solution. Oxidise with HNO_3 or KClO_3 , add soda carbonate to destroy all or nearly all the free acid, taking care to stop the addition short of the production of a red colour or precipitate. Pass through a small pulp filter, place the filter in a flask containing 30–40 c.c. more soda hydrate of strength 2 N than is necessary to precipitate the whole of the iron. This amount is easily calculated if nearly all the free acid has been neutralised, because 1 grm. of iron as Fe_2Cl_6 would require 54 c.c. normal soda to just precipitate it. There is no exceptional advantage in this particular excess of NaHO except that it is sufficient without being wasteful, and large excesses tend to retard subsequent operations.

After disintegrating the added filter, which may possibly contain a little MoO_3 or WO_3 , the contents of the flask are heated nearly to boiling, the flask placed under a funnel with a constricted stem, and violently shaken with one hand, whilst the hot sample is poured through the funnel with the other. The Mo is all in solution, and after fractional filtration and acidification of the clear solution with HCl, the metal is precipitated as PbMoO_4 in the manner already described (*CHEM. NEWS*, lxxviii., 203).

The following table shows how perfect the above separation is. The PbMoO_4 precipitated from the filtrate was always re-dissolved in HCl , a small quantity of SiO_2 separated, and the Mo re-precipitated. Without this precaution, the first precipitation gave results averaging a plus error of 1 per cent:—

Grms. of iron.	Mo added.	Mo found.
0.2	0.2	0.1998
0.5	0.25	0.2485
0.6	0.15	0.1499
0.9	0.10	0.0998
2.0	0.015	0.0151
2.0	0.0025	0.0026
2.0	0.0005	0.00047

Some experimental samples of cast-iron containing from 3 to 4 per cent of Mo were successfully assayed in the above manner, although it is perhaps better to filter off the graphite, burn the filter at low redness, and fuse the residue with KNO_3 . This was advantageous in the particular samples alluded to, because they also contained tungsten in considerable amounts.

The estimation of Mo in steel as carried out by this process is not interfered with by any of the usual elements found in steel, such elements being either precipitated along with the iron or exercising no influence in the subsequent precipitation of the Mo with lead acetate; this remark, of course, does not apply to tungsten. Appended are a few results:—

	Per cent.
Mo found in steel free from Ni and Cr	2.72
Mo found in same steel after adding 20 p.c. Ni. .	2.73
" " " " 20 " Cr. .	2.72
" " " " 20 " Mn. .	2.75

In the case of chromium there was probably a small quantity of chromium in the filtrate as chromate. A few drops of SO_2 solution were added before precipitation. The ammonium acetate which we always add before filtering the boiling mixture effectually holds in solution the small quantity of lead sulphate which might otherwise accompany the PbMoO_4 .

We think it desirable to mention here the results of experiments instituted to determine whether Mo in steel interferes with the estimation of the other elements, and how its interference may be overcome:—

Silicon.—Molybdenum does not interfere.

Manganese.—If estimated by separation of the iron with ammonium acetate and precipitation with Br and ammonia, Mo exerts no influence. Unless a large excess of acetate is used, nearly all the Mo is precipitated with the iron. In the volumetric determination by oxidation with KClO_3 in nitric acid solution, the results are low. A steel with Mn contents of 0.60 per cent gave only 0.39 per cent. By the addition of six instead of three separate lots of chlorate, the full amount of manganese was obtained.

Sulphur.—The gravimetric estimation of sulphur is accurate if the BaCl_2 is added to a distinctly acid solution in order to eliminate the possibility of contamination with BaMoO_4 or basic ferric molybdates. The evolution method, *i.e.*, the dissolution of the steel in HCl , the evolved H_2S being passed through metallic solutions, is also uninfluenced by the presence of Mo. One would expect low results due to the formation of MoS_3 in the evolution flask. This does not seem to be the case when strong HCl is used to effect decomposition.

Phosphorus.—The long (acetate) molybdate method yields accurate results in the presence of Mo. The rapid method, in which the P is precipitated in the presence of all the iron, gives high results, apparently in consequence of contamination of the yellow precipitate with MoO_3 . The difficulty may obviously be overcome by dissolving out in ammonia and precipitating with magnesia mixture.

Carbon.—The carbonaceous residue, after decomposing the sample with copper solutions, gives blue washings

(Mo_3O_8) long after the copper salts have been washed out. The results, compared with direct combustions with PbO_2 or Pb_3O_4 , are a few hundredths per cent too low.

Iron.—On precipitating with ammonia part of the molybdenum accompanies the iron; gravimetric results are therefore too high. The iron cannot be estimated by simply dissolving the sample and titrating, because the molybdenum, reduced by the liberated hydrogen to Mo_2O_3 , falsifies the result by being oxidised to MoO_3 . For a like reason ferric solutions containing molybdenum should not be reduced with zinc or stannous chloride. They may, however, be reduced with SO_2 , and titrated accurately either with bichromate or permanganate. Potassium ferrocyanide does not certainly indicate ferric iron, on account of the very ready formation of a deep brown precipitate with MoO_3 solutions.

Analysis of Ferro-molybdenum and Fused Molybdenum Metal.—These alloys are readily attacked by acids, and analysed as just described.

Analysis of Nickel-molybdenum.—These alloys generally contain very little iron, so that, after decomposing the sample with aqua regia, the solution is poured into an excess of ammonia. If more than a few tenths per cent of iron are present, the precipitate contains small amounts of Ni and Mo, which may be removed by a second precipitation. The Mo may then be precipitated from a portion of the combined filtrates without separating the nickel, and the nickel may be cyanometrically estimated without separating the Mo. Where iron is present in very large amounts, the molybdenum should be separated as for steels, by means of NaHO , and the Ni and Fe separated afterwards in a fresh sample for the estimation of Ni. This latter separation may be effected with the greatest facility by means of ammonia, a process which depends for its success upon the fact that basic ferric molybdate forms when considerably less ammonia is added than would make the solution alkaline.

Nearly every commercial sample of ferro-molybdenum or nickel-molybdenum we have examined contained tungsten amounting to 1 or 2 per cent. A sample of molybdenum-nickel, which was too tough to break and exceedingly difficult to drill, contained 3 per cent of sulphur.

Analysis of Molybdenum Powders.—A comparison of the analysis of these powders as submitted by their vendors, with those representing actual composition, affords the strongest possible evidence of the need of some definite instructions regarding the analysis of them. We have never met with a sample which professed to contain less than 95 per cent of Mo, and have never found one which contained as much as 90 per cent.

An estimation of the separate elements, or combination of elements, which make up a common molybdenum powder, would be a very difficult piece of work, as it may contain, besides metallic Mo, such bodies as MoO_3 , mixtures of the lower oxides of Mo, metallic W, oxides of W, silica, alumina, iron, ferric oxide, combined carbon, graphite or charcoal, sulphur and water in quite appreciable quantities. It is certainly desirable, if powder continues to be the form in which this metal is supplied to steel manufacturers, to have more or less ready means of submitting the material to a complete examination. At present we are disposed to make ourselves responsible only for such processes as may be used to determine the more important constituents.

Carbon.—The total carbon may readily be determined by direct combustion in a current of oxygen. Moissan, in a very interesting paper (CHEMICAL NEWS, lxxii., 2), determines the combined carbon by attacking the sample with acids, passing the gases over copper oxide, &c., into KHO , the graphite being determined in the insoluble residue.

Molybdenum.—For the estimation of the chief element the powder may be mixed with Na_2CO_3 and a little KNO_3 to promote oxidation, placed in a platinum crucible under a layer of Na_2CO_3 , and heated over the blowpipe until

decomposed. Only the bottom of the crucible should be kept red-hot, so as to avoid volatilisation of any MoO_3 . After extracting with water, the Mo and W are precipitated in the filtrate from the insoluble Fe_2O_3 , &c., with lead acetate, and separated as described by us (CHEMICAL NEWS, lxxxi., 13).

A more complete examination of the sample is possible if 3 to 5 grms. are opened out with aqua regia, the solution being evaporated dry, and the residue well boiled with concentrated HCl, diluted, and filtered. The residue, after ignition at low redness, may contain WO_3 , SiO_2 , and MoO_3 . It is fused with KNO_3 , and the aqueous extract added to the main filtrate or analysed separately. A portion of the main filtrate is used for estimating the Mo and W after separating the small amounts of iron and alumina with ammonia. Another portion may be used for estimating sulphur, and so on.

Oxygen.—The better qualities of powder supplied to steel-makers are grey and anhydrous; the poorer qualities are black, and may contain 5 to 6 per cent of water. Owing to imperfect reduction in the first instance, or subsequent decomposition, assisted perhaps by exposure, molybdenum powders may contain, besides the metal itself, its oxides Mo_2O_3 , MoO_2 , MoO_3 , and Mo_3O_8 . We are unable to supply a satisfactory method for the estimation of these oxides separately, and think it hardly worth the trouble which would be involved, in view of the probable substitution for the powder of fused metal or metallic alloys for steel-making purposes.

The blue oxide (Mo_3O_8) or its hydrate is soluble in water, so that merely shaking the sample with water serves to identify it; it is frequently present in the moist black powders. For the rest we have obtained a useful figure by boiling 1 grm. of the sample for five to ten minutes with 100 c.c. of a bi-normal solution of caustic potash, filtering, and precipitating the Mo in the filtrate. The oxygen is then calculated on the supposition that the Mo dissolved out existed as MoO_3 . Metallic Mo is practically insoluble in potash, and, according to Comey's Dictionary, so also are Mo_2O_3 and MoO_2 ; hence the figure obtained would always err on the negative side.

The treatment with KHO occasionally results in the formation of a precipitate of lead sulphide in the filtrate when lead acetate is added for the estimation of the Mo. In such a case one must of course expel the H_2S from the acidified filtrate before precipitating.

Both Mo and MoO_2 reduce ammoniacal silver solutions, six atoms of silver being, according to E. F. Smith (*Journ. Chem. Soc.*, lxiv., p. 171), replaced by one of Mo. As silver can be estimated so easily and accurately the indirect estimation of the oxygen of a Mo powder by these means appeared promising. Unfortunately, however, with such highly carburetted (and sometimes sulphuretted) material as these powders, the results are always too high. One can of course distinguish a sample poor in metallic Mo from a rich one, but so far as a single sample is concerned the result forms only a rough test.

The following are typical analyses of commercial molybdenum alloys. I. and II. are molybdenum powders; III. and IV., MoNi alloys; V., a ferro-molybdenum; and VI., fused molybdenum metal.

	I.	II.	III.	IV.	V.	VI.
Mo	72.62	86.72	70.53	36.75	16.69	92.40
W	3.17	nil	1.27	—	1.53	0.74
Ni	—	—	21.60	57.80	—	—
Fe	1.60	0.48	3.08	1.60	76.34	2.73
C	7.80	8.18	2.94	1.08	4.20	3.87
Si	—	—	0.42	0.14	0.39	0.05
SiO ₂	—	1.57	—	—	—	—
Mn	—	nil	0.40	trace	0.37	nil
S	—	0.10	trace	3.00	0.076	0.33
O	8.30	1.00	—	—	—	—
H ₂ O	4.30	—	—	—	—	—

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ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.*

By LILY G. KOLLOCK.

(Concluded from p. 246).

BISMUTH.

SMITH and Thomas (*Am. Chem. Journ.*, v., 114) deposited bismuth from a citrate solution which contained an excess of sodium citrate. Bismuth hydroxide was dissolved in citric acid and sodium hydroxide added to alkaline reaction. Smith ("Electro-chemical Analysis," p. 69) also states that bismuth may be precipitated from an alkaline citrate solution and a solution containing free citric acid. The conditions under which the deposition took place are not recorded. The following experiments were accordingly made in order to obtain the proper working conditions:—

Bismuth from an Ammonium Citrate Solution.—A bismuth nitrate solution was made, adding sufficient nitric acid to the salt to prevent the formation of a basic nitrate on the addition of water. To a solution of this salt containing 0.1882 grm. of metallic bismuth were added 3 grms. of citric acid, and the solution made ammoniacal. It was diluted to 125 c.c. The temperature was raised to 70° C. A current of $\text{N.D.}_{100}=0.02$ A and $\text{V}=1.8$ was allowed to act for three hours. At the expiration of this time the current was increased to $\text{N.D.}_{100}=0.04$ A and $\text{V}=2.3$. Finally, in order to deposit the last traces of the metal held in solution, the current was made $\text{N.D.}_{100}=0.09$ A. The deposit of bismuth obtained in this way was light grey in colour, very compact, and adherent. In one case the current acted all night, and the deposit was darker in colour, but adherent and easily washed. There was a noticeable amount of the bismuth peroxide deposited. The anode was weighed therefore before and after the electrolysis, and from the weight of the bismuth peroxide found, the amount of the bismuth deposited in this way, calculated and added to the weight of that precipitated upon the cathode (see Table XXIV.).

Bismuth from a Potassium Citrate Solution.—The solution of bismuth nitrate used contained 0.1777 grm. To this were added 7 grms. of citric acid, followed by an excess of potassium hydroxide. The solution was diluted to 125 c.c. The temperature was 70°. The current for this solution was also low at the beginning and was gradually increased to 0.09 A. The deposit of bismuth peroxide on the anode was treated as indicated in the preceding method. The bismuth was in all cases a grey compact adherent deposit (see Table XXV.).

Bismuth from a Citric Acid Solution.—Seven grms. of citric acid were added to a solution of bismuth nitrate containing 0.1767 grm. of bismuth. The solution at 70° was electrolysed with a current $\text{N.D.}_{100}=0.02$ A and $\text{V}=1.8$. Subsequently it was increased to $\text{N.D.}_{100}=0.07$ A and $\text{V}=2.6$ (see Table XXVI.).

Mercury from Nitric Acid Solution.—The fact that mercury could be determined satisfactorily from a nitric acid solution appears in the *Berichte* (xix., 329). Mercuric nitrate was electrolysed by Smith and Knerr (*Am. Chem. Journ.*, viii., 206). There was $\frac{1}{2}$ to 1 c.c. of free nitric acid present. Bright shining deposits of 0.091 grm. were obtained in thirty minutes. The current used for the purpose liberated 4 c.c. of oxyhydrogen gas per minute.

In the following work 3 c.c. of concentrated nitric acid were added to a solution of mercuric chloride containing 0.1403 grm. of metallic mercury. The solution (125 c.c.) was electrolysed with a current $\text{N.D.}_{100}=0.06$ A and $\text{V}=2$ for four hours. The temperature was 70° C. The solution in the dish was syphoned off before the interruption of the current (see Table XXVII.).

Mercury from Sulphuric Acid Solution.—It has been known for a considerable time that mercury could be

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xxi., No. 10.

TABLE XXIV.

Bismuth. Grm.	Citric acid. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Amount found. Grm.
0.1882	3	125	N.D. ₁₀₀ =0.02 (for three hours.) N.D. ₁₀₀ =0.04 A. " =0.06 A.	1.8 2.3	70° All night in cold.	16	0.1881
0.1882	3	125	" =0.02 A. (for three hours.) N.D. ₁₀₀ =0.04 A. " =0.09 A.	1.6 2 3	70°	6½	0.1880
0.1882	3	125	" =0.03 A. " =0.042 A. " =0.09 A.	2 2.58 3	65°	6	0.1819
0.1882	3	125	" =0.03 A. " =0.042 A. " =0.09 A.	2 2.6 3	65°	6	0.1820

TABLE XXV.

Bismuth. Grm.	Citric acid. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Amount found. Grm.
0.1767	7	125	N.D. ₁₀₀ =0.02 A.	2.16	65°	5	0.17648
0.1767	7	125	" =0.038 A.	2.18			
0.1777	7	125	" =0.02 A.	2.5	70°	5	0.1781
0.1777	7	125	" =0.05 A.	3			
0.1777	7	125	" =0.03 A.	2.1	65°	5½	0.1774
0.1777	7	125	" =0.05 A.	2.5			

TABLE XXVI.

Bismuth. Grm.	Citric acid. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Amount found. Grm.
0.1767	7	125	N.D. ₁₀₀ =0.02 A.	1.8	65°	5	0.17648
0.1767	5	125	" =0.038 A. " =0.02 A. " =0.05 A.	2.6 1.8 2.66	70°	5	0.1761

TABLE XXVII.

Mercury. Grm.	Nitric acid. C.c.	Dilution. C.c.	Current.	Voltage.	Temperature.	Time. Hours.	Amount found. Grm.
0.1403	3	125	N.D. ₁₀₀ =0.06 A.	2	70°	4½	0.1404
0.1403	3	125	" =0.07 A.	1.91	70°	4	0.1406

TABLE XXVIII.

Iron. Grm.	Citrate. Grms.	Citric acid. Grm.	Current.	Voltage.	Temperature.	Time. Hours.	Found. Grm.	Carbon. Per cent.
0.0378	10 c.c.=1.18	3 c.c.=0.059	N.D. ₁₀₀ =0.58 A.	5.7	35°	7	0.0379	0.079
0.0378	10 c.c.=1.18	3 c.c.=0.059	N.D. ₁₇₅ =8-1.3	9-11	70°	4	0.0383	1.1
0.1035	10 c.c.=1.18	3 c.c.=0.059	N.D. ₁₇₅ =8	9-11	50°	4½	0.1046	1.06
0.1277	10 c.c.=1.18	5 c.c.	N.D. ₁₀₀ =0.4-1 A.	7-11	50°	4½	0.1278	0.00
0.1277	10 c.c.=1.18	5 c.c.	" =0.8 A.	7-8	50°	4½	0.1280	0.94

deposited from a solution feebly acidulated with sulphuric acid. The current which was used generated 5 to 6 c.c. of oxyhydrogen gas per minute. In repeating this method for the precipitation of mercury, 1 c.c. of sulphuric acid was added to a solution of mercuric chloride. A current of N.D.₁₀₀=0.4-0.6 A and V=3.5 effected the deposition. The temperature during the operation was 65° C. The mercury was entirely deposited in one hour; it had a brilliant metallic appearance; it was washed with cold water. The mercury present in the solution was 0.1403 gm. The deposit weighed 0.1402 gm.

Iron from a Citrate Solution.—In 1888 Smith reported the deposition of iron from a sodium citrate solution con-

taining free citric acid. The solution used was ferric ammonium sulphate, and the current acting upon the solution gave 6 c.c. of oxyhydrogen gas per minute.

The method was repeated, using a solution of the alum containing 0.0378 gm. of metallic iron, 10 c.c. of sodium citrate (equivalent to 1.18 grms.), and 3 c.c. of citric acid (equivalent to 0.059 gm.), and the solution diluted to 125 c.c. With a current of N.D.₁₀₀=0.58 A and V=5.7 in seven hours the deposition was complete. Another determination gave 0.0375 gm. of iron, and a third gave 0.0379 gm. By titration with potassium permanganate the deposit was found to contain 0.03789 gm. of iron. The carbon therefore in this deposit was 0.079 per cent.

Similar experiments were conducted, using 0.1035 grm. of iron. The current used was N.D.₁₇₅=0.8 A and V=9. The temperature was 60° during the electrolysis. The solution was 250 c.c. The deposit weighed 0.1046 grm. By titration of the iron, 1.06 per cent of carbon was found. With identical conditions, using 0.1280 grm. of iron, 0.94 per cent of carbon was found deposited in the metal (see Table XXVIII.).

NOTE ON THE ESTIMATION OF NICOTINE, AND ON THE AMOUNT OF NICOTINE IN NEW SOUTH WALES TOBACCOS.*

By G. HARKER, B.Sc.

KISSLING's and Biel's methods for nicotine were compared and found to give similar results. The generally accepted statement that nicotine is lost from its ethereal solution during evaporation was not found in accord with the results obtained in this investigation. An alternative method given by Biel, in which the weight of the double sulphates of nicotine and ammonia was employed, was found to be practically worthless, as a constant weight cannot be obtained. Several attempts, all of which occupied much time, were made to estimate nicotine volumetrically in an aqueous solution containing nicotine and ammonia, but owing to the close similarity in the properties of these substances the attempts were not successful. Four varieties of New South Wales tobaccos were analysed for nicotine, with the following result:—

Manilla	1.95 per cent
Tamworth	2.36 "
Tumut	3.84 "
Bathurst	4.53 "

THE RELATION OF THE TASTE OF ACID SALTS TO THEIR DEGREE OF DISSOCIATION.

By LOUIS KAHLENBERG.

INVESTIGATIONS on the taste of dilute solutions of acids, when regarded in the light of the theory of electrolytic dissociation, have yielded the general result that sour taste is due to hydrogen ions, and that its intensity varies as the concentration of the hydrogen ions in the solution. According to Richards (*Amer. Chem. Journ.*, xx., 121), sulphuric, nitric, hydrobromic, and hydrochloric acids can still be detected by the sense of taste in solutions somewhat less than $n/1000$. My own tests place the limit at $n/800$, at which dilution the taste is only astringent, while at $n/400$ it is slightly sour. It will be seen from this that the sense of taste is indeed a fairly delicate means of detecting acidity. Richards observed that while the sour taste of tartaric, citric, and acetic acids diminishes in the order named, and hence agrees qualitatively with the dissociation theory, the quantitative agreement is not satisfactory, acetic acid, for instance, having a sour taste at least as strong as hydrochloric acid of one-third the equivalent concentration, whereas the former acid is dissociated to only about one fourteenth the extent of the latter. The results of my tests (L. Kahlenberg, *Bull. Univ. of Wis.*, ii., 1—31; ref. *Journ. Phys. Chem.*, 1899, iii., 66; *Zeit. Phys. Chem.*, 1899, xxix., 343), with acetic acid are similar to those of Richards, for I found that acetic acid has about four times as sour a taste as one would expect according to the dissociation theory.

The object of this article is to investigate the taste of the acid sodium salts of a number of dibasic organic acids, and also of the acid salts of citric acid, and to view the results in the light of the theory of electrolytic dissociation.

The acid sodium salts of the following acids were tested: Oxalic, malonic, succinic, malic, tartaric, fumaric, maleic, and citric. The method of investigation was as follows: Solutions containing 1 grm.-molecule of the acid salts in 100 litres were prepared; these were diluted successively with equal volumes of water. All of the solutions were tasted by myself by holding 6 to 8 c.c. in the mouth for a few months after it had been well rinsed with distilled water. Of course the results can not claim to be as free from bias as those that were obtained in my former investigations, where a number of persons who were entirely ignorant of the nature of the substances they were tasting, tasted the solutions. My previous work, however, has taught me that my own sense of taste is what one would call normal; and the data given below I deem perfectly reliable, as I did not work with solutions so dilute that their taste was not clearly defined. The taste of solutions of the acid sodium salts of malic and tartaric acids was compared with that of a very dilute solution of hydrochloric acid of known strength. In these tests the method of experimentation employed in my previous investigations (*loc. cit.*), was strictly followed, five persons serving as subjects. The results of these tests are also given below.

The degree of the hydrogen dissociation of acid sodium salts has been determined by means of the method of sugar inversion by J. E. Trevor (*Zeit. Phys. Chem.*, 1892, x., 321), and also more recently by W. A. Smith (*Zeit. Phys. Chem.*, 1898, xxv., 217). The figures found are, as is well known, surprisingly low. The following table gives the percentage of hydrogen dissociation in the case of the acid sodium salts in question, and also the volume in litres in which 1 grm. of hydrogen ions is contained. With the exception of the figure for oxalic acid, the results are those of Smith. With but few exceptions the results of Trevor and those of Smith agree tolerably well. For the present purpose it is immaterial whether the results of the one or those of the other be used, as the general conclusion would remain the same.

Acid sodium salt of—	H dissociation in per cent	
	when 1 grm.-mol. is present in 128 litres.	1 grm. H ions is contained in—
		Litres.
Oxalic acid.. ..	4.37	2929
Malonic „	0.50	25600
Succinic „	0.159	80500
Malic „	0.719	17800
Tartaric „	2.800	4571
Fumaric „	1.52	8421
Maleic „	0.55	23273
Citric „	—	—
Mono Na salt	1.92	6666
Di Na salt	0.060	213333

Assuming that sour taste is due to hydrogen ions, it follows from these results (and the fact above mentioned, that the sense of taste is able to detect the presence of the strong mineral acids at no greater dilution than 1 grm.-molecule in 1000 litres) that none of the salts given in the table ought to have any sour taste at all when 1 grm.-molecule is contained in 128 litres. Now as a matter of fact they all have a sour taste at this dilution, and some of them even at much higher dilutions, as the following data show.

Acid sodium oxalate is very plainly sour at the concentration 1 grm.-mol. in 200 litres, and even at 1 grm.-mol. in 400 litres it is still distinctly, though of course faintly, sour.

Acid sodium malonate is distinctly, though slightly, sour at 1 grm.-mol. in 200 litres; while at 1 grm.-mol. in 400 litres it is slightly astringent.

A solution of acid sodium succinate containing 1 grm.-mol. in 200 litres is still distinctly sour, but it also has the disagreeable taste characteristic of the free acid.

Acid sodium malate is distinctly sour at 1 grm.-mol. in 200 litres, but slightly astringent at 1 grm.-mol. in 400 litres.

* Abstract of a Paper read at the Melbourne Meeting of the Australasian Association for the Advancement of Science, Jan., 1900.

A sodium bitartrate solution containing 1 grm.-mol. in 200 litres is very distinctly sour; while at 1 grm.-mol. in 400 litres it is astringent or very slightly sour.

Acid sodium fumarate is distinctly sour at 1 grm.-mol. in 100 litres, and still plainly, though faintly, sour at one-half this strength. At 1 grm.-mol. in 400 litres is slightly astringent.

The acid sodium salt of maleic acid tastes sour at 1 grm.-mol. in 100 litres, and it has in addition the disagreeable taste characteristic of maleic acid. At 1 grm.-mol. in 200 litres the acid salt has a slightly astringent effect.

Mono-sodium citrate is very plainly sour at 1 grm.-mol. in 100 litres; while at 1 grm.-mol. in 400 litres it is weakly but still distinctly sour. At one-half the latter strength the solution is very faintly sour or astringent.

Di-sodium citrate is slightly sour at 1 grm.-mol. in 100 litres; while at one-half this concentration it is very faintly sour or simply astringent.

In addition to this, I found by direct tests* on five persons that a solution of acid sodium malate of 1 grm.-mol. in 50 litres is about as sour as a solution of hydrochloric acid containing 1 grm.-mol. in 140 litres; again, a solution of acid sodium malate of 1 grm.-mol. in 100 litres is about as sour as a solution of hydrochloric acid of 1 grm.-mol. in 320 litres. A solution of sodium bitartrate containing 1 grm.-mol. in 100 litres is as sour as a solution of hydrochloric acid containing 1 grm.-mol. in from 280 to 300 litres. A difference in the quality of the tastes of these dilute solutions of hydrochloric acid and the sodium bimalate and sodium bitartrate respectively could not be detected by the persons tested or by myself.

It is clear from the facts presented that the sour taste of solutions of these acid sodium salts can not be ascribed to the hydrogen ions present, for there are too few of them. The question then arises—to what is the sour taste of these solutions due? Looking at the matter from the standpoint of the theory of electrolytic dissociation, the undissociated molecules and also the bivalent anions in the solutions in question are relatively very few in number, while sodium ions and monovalent anions of the

general formula HAc are abundant. Now as sour taste is not produced by sodium ions (for solutions of the normal sodium salts have no sour taste), it follows that it must be ascribed to the monovalent anions. We are led to the conclusion, then, that these particular anions produce upon the sense of taste an effect that is identical with that produced by hydrogen ions. It should be borne in mind in this connection that these anions are large complexes varying in chemical composition in the case of different salts, that they bear electrical charges opposite to those on hydrogen ions, and that they are much less mobile than the latter. It is therefore evident that the explanation of the sour taste of the solutions of these acid salts from the standpoint of the theory of electrolytic dissociation is unsatisfactory to say the least.—*Journal of Physical Chemistry*, iv. No. 1.

CORRESPONDENCE.

SYNTHESIS OF ARSENIC.

To the Editor of the Chemical News.

SIR,—On page 257, col. 2, lines 9 and 10 of the current volume of the *CHEMICAL NEWS*, I read:—" [Note by Translator. — There is evidently an error in these figures]. " Allow me to point out that the figures given, viz., the percentage of arsenic yielded by certain weights of phosphorus, are perfectly correct.—I am, &c.,

ANALYST.

London, W., June 2, 1900.

* These experiments were conducted in the same way that my previous tests on taste were made (i. e.), so that a detailed description is hardly necessary in this connection.

NOTICES OF BOOKS.

Geber; A Tale of the Reign of Harun al Raschid, Khalif of Baghdad. By KATE A. BENTON. New York: Frederick A. Stokes Company. 1900. Pp. 487. 8vo.

THE name Geber brings to mind those noted chemical treatises that for four centuries have been attributed to the famous Arabian physician, but which Berthelot has shown to be fraudulent. In the romance before us Mrs. Benton has taken the astrologer and physician as a central figure, and has grouped around him historical personages and imaginary characters in a sumptuous oriental setting.

The characters of the famous Khalif and of Jaafer the Barmecide and his family closely follow the lines of history, but the events which led to the rupture of the friendship between Harun and Jaafer, and the consequent downfall of the latter's family, while mainly historically correct, contain much that is fiction.

The story opens with the call of the physician Geber to Damascus, where the favourite wife of the Khalif is suffering from a mysterious malady; the astrologer, who has his own reasons for enmity against Harun, sees in the call an opportunity to work a long meditated revenge, obeys the summons, and with his family and servants takes up his abode in the magnificent capital of the Khalif's dominions, earning his gratitude and many privileges by effecting an immediate and remarkable cure.

The wily astrologer makes good use of his advantages, and slowly weaves a web around Harun wounding him in all his most vulnerable points, and finally making him believe that his dearly beloved wife is unfaithful, and his trusted friend is his betrayer.

The interest is well sustained, although the great numbers of characters introduced is sometimes confusing to the reader. Several love stories run their course through the book, two of which, after due allowance of danger and difficulty, end in the orthodox happy manner.

Of genuine alchemy, either theoretical or practical, the book contains little, the romantic side of the period being that which is more fully developed by the gifted author; there are, however, several scenes in which astrology and catoptronomy play their part.

Perhaps the weakest incident in the book, because most improbable and at variance with what the writer has shown to be the true character of the leading figure, is the closing scene, where Geber having accomplished his revenge and seen his desire upon his enemies, sparing none who stood in the way of his purpose, becomes a Christian and dies with words of repentance and charity upon his lips.

The book has a pathetic interest, the author having died while it was going through the press. There is a bibliography of authors and the volume shows the result of much painstaking study. Some reviewers have pronounced the book to be one of the most fascinating stories published during the year.

Flame, Electricity, and the "Camera." Man's Progress from the First Kindling of Fire to the Wireless Telegraph and the Photography of Colour. By GEORGE ILES. New York: Doubleday and McClure Co. 1900. Pp. xv.—398, 8vo. Ill.

To trace man's progress in applied science from the first kindling of fire to the latest discoveries made in the year 1899 is a vast undertaking, but Mr. George Iles is to be congratulated on the manner in which he has accomplished the task: he has produced a book as fascinating to the student of science and of civilisation as a clever romance is to a reader of good fiction, and he has been fortunate in finding a publisher who knows that a strong book deserves a handsome dress.

Mr. Iles is a pronounced evolutionist, and writes from that standpoint; the main argument of the book was indicated by the author in the *Popular Science Monthly* for June, 1876. He claims that progress in scientific discovery obeys a law of permutative multiplication, that here and there the progress of humanity has made leaps, and three of the most prodigious bounds were made when heat, electricity, and the camera became the servitors of the race. In portraying this conception he is fortunate in possessing a charming and forcible diction, while he rarely neglects a small point which can strengthen his argument. Indeed very little seems to have escaped close study; he is equally at home in describing the mastery of metals, the conversion of heat into motive power, the methods of producing electricity from the first beginnings to the latest improved apparatus; special instruments, such as the telephone, the kinoscope, and the bolometer, as in depicting the forward march of the sciences underlying these, and their application to everyday life.

In a book covering so enormous a range, condensation is of course a prime necessity, but Mr. Iles is never obscure: he has the faculty of generalising as well as of specialising, and, whether he is describing the problems of multiplex telegraphy, or those of colour photography, the discovery of Röntgen's X-ray, or the history of Cyrus Field's courage in laying the Atlantic cable, he never fails to interest the reader.

The author means to be impartial, and if he brings into prominence the work of Americans in the diverse fields, can he be blamed? Especially as they are sometimes neglected by Europeans writing on the history of science. He has been a careful student of the chronology of facts, but the reviewer believes that on page 271 he gives credit to Porta for discoveries made long previously by the wonderful man Leonardo da Vinci.

The volume is not a history, yet it contains much history; it is not a text-book in any sense, yet it could be most advantageously read by students of science; it is not a romance, yet it treats in most agreeable language of the romantic side of science.

It is interesting to note how very recent in date are the occasional citations; one gives statistics as late as December, 1899. This is only an indication of the up-to-date-ness of the whole work. Ninety-three illustrations and twenty-two superior plates illustrate the volume; the portraits of Volta, Faraday, Lord Kelvin, Edison, Niepce, Daguerre, and the artistic plates, are of the best.

No one who cares to inform himself as to the steps by which modern civilisation has reached its present plane can afford not to own this remarkable book.

H. C. B.

Practical Methods for Determining Molecular Weights.
By HENRY BILTZ. Translated by H. C. JONES and S. H. KING. Easton, Penna.: The Chemical Publishing Company.

THE subject of this work is, as its title implies, a description of the theory and practice of the various methods devised for the determination of molecular weights. Some of these have been well known for many years, whilst others have been more recently devised, and are still buried in technical periodicals and pamphlets.

The first method treated, that of vapour density, depends on Avogadro's law, that, at a given pressure and temperature, an equal number of molecules of all gases occupy the same volume. This was early developed, on two different lines, by Gay-Lussac and Dumas; both being limited in their range of application, were superseded by V. Meyer's method of gas displacement. A useful list of liquids suitable for employment in the vapour-jacket, at various temperatures, appears on page 18. Hofmann's method of mercury displacement is also described, though it is seldom used nowadays.

The second method described is the Osmotic. This has been principally applied in three different manners, viz., (1) the freezing-point method; (2) the boiling point method; (3) Nernst's method of observing the lowering of solubility. These are treated at great length, and their uses and limitations fully set forth; the principal objection is that the molecular weight cannot be directly determined by these means, but must be arrived at by extrapolation on the curve of plotted results.

Traube's method, discovered and worked out in the years 1895-6, requires a pre-knowledge of the composition of the substance under investigation and an approximate knowledge of its formula. There is at present no theoretical foundation for this method; the principle upon which it depends is this:—"An increase in volume takes place when a molecule is formed from atoms; this is independent of the chemical nature of the substance, and can be only slightly modified by constitution. It amounts to 25.9 c.c. for a gram-molecule at 15° C."

The book is worthy of a place in all laboratories where general analytical work is being carried on.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal de Pharmacie et de Chimie,
Series 6, Vol. xi., No. 5.

Analysis of Water from Jouhe, near Dôle (Jura).—Paul Bourcet.—The waters of Jouhe come from a source of which the therapeutic value has been widely spread in the neighbourhood. Though famous so long ago as the year 1710, it appears that nothing was known definitely as to the composition and saline richness of these waters; the author has therefore made an analysis. The sample was taken on August 17, 1899; the temperature of the water was +12.7°, the temperature of the air being +22.7°; its appearance was clear, and it had a slight sulphurous smell. One litre of water gave off, when boiled, 29.2 c.c. of gas at 760 m.m. B.P. and 15° C. The composition of this gas was found to be:—

	Per cent.
Carbonic acid	29.35
Oxygen	7.32
Nitrogen	61.16
Marsh gas	2.17

and a trace of sulphuretted hydrogen. After evaporation, this water left a residue weighing 2.8347 grms., of the following composition:—

	Grms.
Chloride of sodium	1.3203
Chloride of magnesium	0.2596
Bicarbonate of magnesia	0.0105
Sulphate of lime	0.9973
Bicarbonate of lime	0.2498
Carbonate of iron	0.0004
Silica	0.0097
Iodine	traces
	2.8476

In spite of the local opinion, this water is not sulphurous. The faint odour of sulphuretted hydrogen which it possesses comes from a slight decomposition of the sulphate of lime by the organic matter present.

Composition of Essence of Santal from the East Indies.—M. Guerbet.—The result of a large number of experiments on the composition of essence of santal may be represented approximately in the following manner:—

Santalenes α and β	60
Santalols α and β	800
Santalal	30
Acids in the form of ethers (formic, acetic, santalic, teresantalic)	30
Undetermined products, with a powerful odour, boiling at 130–220°	3
Undetermined products, boiling at about 320° and over (carbides, alcohols, ether oxides, resinous product-)	77
	1000

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 2.

The Action of Mercury on Iodide of Methylene.—V. Thomas.—Already inserted.

Preparation of Carbazides. Action of Hydrazines on the Phenolic Carbonates.—P. Cazeneuve and M. Moreau.—When 25 grms. of hydrazine in solution in 25 grms. of water are poured into 25 grms. of carbonate of phenyl, the mixture becomes very hot and the carbonate dissolves. On cooling, a magnificent crop of crystals of phenate of hydrazine are obtained, which melt at 63–64°, and by analysis correspond with a compound of four molecules of phenol to one molecule of hydrazine, $(C_6H_5O)_2NH_2-NH_2(C_6H_5O)_2$. This phenate is easily decomposed. When one molecule of phenylic carbonate, or 25 grms., is heated for an hour to 160–170° with four molecules of phenylhydrazine, or 50 grms., traces of CO_2 are given off, and the liquid gradually becomes yellow. On cooling, a yellowish white crystalline mass is obtained, which is taken up warm with 200 grms. of alcohol at 60° made strongly acid with hydrochloric acid to remove the excess of phenylhydrazine. After two re-crystallisations, a body is obtained, melting at 169–170°, corresponding to $CO<\begin{smallmatrix} NH-NH-C_6H_5 \\ NH-NH-C_6H_5 \end{smallmatrix}$. In a similar manner two other bodies are obtained by heating together methyl-diphenylhydrazine with carbonate of phenyl and naphthylhydrazine β with phenylic carbonate. This first one, having the formula $CO<\begin{smallmatrix} NH-NCH_3-C_6H_5 \\ NH-NCH_3-C_6H_5 \end{smallmatrix}$, melts at 149–150°, and cannot be distilled without decomposition; the second body, $CO<\begin{smallmatrix} NH-NH-C_{10}H_7 \\ NH-NH-C_{10}H_7 \end{smallmatrix}$, does not melt without decomposition.

Transformation of the Acetic Ethers of Ordinary Phenol, Paracresol, and Thymol into Benzoic Ethers.—F. Bodroux.—Fifteen grms. of chloride of benzoyl were placed with 10 grms. of acetate of phenyl in a flask of 200 c.c. capacity. A few grms. of powdered zinc were added to the mixture; at first nothing happened, but after a time the mixture warmed up and a violent reaction took place, giving rise to an abundant disengagement of hydrochloric acid. This soon stops, and the product, when left to itself, becomes solid in a few hours. This solid body, after drying, is dissolved in equal parts of warm alcohol and water, and on cooling forms large colourless prisms melting without decomposition at 69°; this body has been identified as benzoate of phenyl. This manner of acting in the presence of zinc powder is not peculiar to acetate of phenyl only; the same reaction takes place with the acetic ethers of paracresol and thymol, and the author has obtained the benzoic ethers of these two phenols. On the other hand, with acetate of naphthol β there is no reaction produced except towards 80°, but this is due simply to the decomposition of the chloride of benzoyl by the zinc, and at the end of the operation the acetic ether can be recovered unchanged.

Naphthopurpurine, a Product of the Oxidation of Naphthazarine.—G. F. Jaubert.—Already noticed.

Volumetric Estimation of the Benzenic Quinones.—

A. Valeur.—Already noticed

MISCELLANEOUS.

University of London.—Rogers Prize.—At a meeting of the Senate of the University of London, held on March 28th, 1900, it was resolved that one sum of £100 be offered as the Rogers Prize open for competition to all the members of the medical profession in Great Britain and Ireland, for an essay under the following regulation as to the subject and conditions thereof, namely:—An essay by any member of the Medical Profession in Great Britain and Ireland upon the "Production of Immunity in Specific Infective Diseases"; generally, and with particular reference to any one disease on which the writer of the essay has made original investigations. The essay is to be sent to the Registrar, University of London, South Kensington, S.W., on or before June 1st, 1901.

The Synthesis of Chrysine.—MM. Emilewicz, Kostanecki, and Tambor.—The authors effected the synthesis of chrysine in the following manner:—They reacted with the ethylic ether of benzoic acid on the trimethylic ether of phloracetophenone in the presence of metallic sodium; a 8-diketone is formed, this and the 2.4.6-trimethoxybenzoylacetophenone under the influence of hydriodic acid are demethylated, and by the closing of the chain is transformed into chrysine. The chrysine thus obtained (1,3-dioxyflavone), $C_{15}H_{10}O_4$, has exactly the properties of the chrysine described by Piccard, but to characterise it and identify it still better with this compound, the authors have prepared tecto-chrysine with their product (1-oxy-3-methoxyflavone), $C_{16}H_{12}O_4$, which has the fusion point expected, viz., 163°, and crystallises in benzene, as shown by Piccard, in large sulphur-yellow crystals. These crystals will be measured. The authors propose to generalise the reaction which has led them to this interesting synthesis, and they rightly point out the value of the services rendered by Piccard to this subject, when he examined and described the colouring matters in poplar buds.—*Berichte*, xxii., p. 2448.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Society of Chemical Industry, 8. "The Maintenance of Aeration as a Standard of Purity of Sewage Effluents," by W. J. Dibdin, F.I.C., F.C.S., and G. Thudichum, F.C.S. "The Composition and Determination of Cerium Oxalate," by Frederick B. Power, Ph.D., and Frank Shedden, B.Sc. "The Production of Nitrate of Soda in Chili," by F. G. Welch.

Royal Institution, 5. General Monthly Meeting.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2116.

VAPOUR-DENSITY OF BROMINE AT HIGH TEMPERATURES.*

(SUPPLEMENTARY NOTE).

By E. P. PERMAN, D.Sc., and G. A. S. ATKINSON, B.Sc.

THE authors regret that they had overlooked a monograph by C. Langer and V. Meyer, entitled "Pyrochemische Untersuchungen," containing an account of some experiments on the vapour-density of bromine. Their method was to pass a mixture of bromine vapour and nitrogen into a porcelain tube with capillary ends placed in a furnace in a horizontal position. The bromine and nitrogen were then displaced by a current of carbon dioxide, the bromine being absorbed by potassium iodide solution, and the carbon dioxide by potash solution, while the nitrogen was collected and measured. Temperature was ascertained by displacing the tube full of air in a similar way. By this method Langer and Meyer carried out experiments at "Zimmer-temperatur," 100°, 900°, and 1200°.

The only results comparable with the authors' are those at 900°. Their results at this temperature are 5'478, 5'414, 5'433, 5'382, 5'59; mean, 5'459 (air=1), or 78'88 (H=1). They say that these results indicate that the vapour-density of bromine, even when diluted with eleven times its volume of air, is still normal at 900°.

The mean of our results at this temperature is 78'6, and the density read from the curve (*Roy. Soc. Proc.*, vol. lxvi., p. 17) is 78'8. This close agreement shows that Langer and Meyer's results really indicate a small amount of dissociation at 900°. Diminution of pressure appears to have little effect at that temperature, as Langer and Meyer used bromine much diluted with nitrogen, while in our experiments there was no decrease of density on reducing the pressure from 767 m.m. to 365 m.m.

It may be noted that Langer and Meyer give the boiling-point of bromine as 63°, whereas we have found the boiling-point of specially purified samples to be very close to 58'9°. (See Ramsay and Young, *Trans. Chem. Soc.*, vol. xlix., p. 454, *et seq.*).

TESTING MINERALS WITH ORGANIC ACIDS.

A CLAIM FOR PRIORITY.

By H. CARRINGTON BOLTON, Ph.D.

THE *Journal of the American Chemical Society* for March, 1900, contains a paper by Joseph W. Richards and Norman S. Powell, entitled, "Substitutes for Hydrochloric Acid in Testing Carbonates"; the authors find that potassium acid sulphate, oxalic acid, citric acid, and tartaric acid can be used in testing carbonates, producing effervescence more or less actively, and they give a table of results. The authors make no reference to previous work on the same lines, and this prompts me to make the claim that about twenty years ago I anticipated all their observations, and published the results in periodicals accessible to every one.

Between 1877 and 1882 I published three memoirs under the title, "Application of Organic Acids to the Examination of Minerals," in which I showed the action of these acids on 200 mineral species, including carbonates, sulphides, oxides, silicates, and many others. I

pointed out the usefulness of citric acid as a substitute for hydrochloric acid in the laboratory and in the field, and showed that by means of it certain minerals could be readily distinguished.

These papers were printed in whole or in part in the following journals:—*CHEM. NEWS*, vols. xxxv., xxxvi., xliii., and xlvii.; *Annals N. Y. Acad. Sciences*, vols. i. and ii.; *Proceedings Amer. Assoc. Adv. Science*, vol. xlvii.; *Reports Brit. Assoc. Adv. Sci.*, vol. i.; *Mineralogical Magazine*, vol. iv.; *Berichte d. D. Chem. Gesellschaft*, vol. xiii.; and abstracts appeared in many other journals. Moreover, the use of citric acid in testing minerals was adopted by teachers in more than one scientific school; the use of potassium acid sulphate having been known long before. Finally, Nason's edition of Elderhorst's "Manual of Qualitative Blowpipe Analysis" (1881) gives a whole chapter to my methods.

It is gratifying to note that the results obtained by Richards and Powell agree well with mine. Coincidences of independent thought often occur, but in publishing a research some acknowledgment of a previous work is generally made; had the authors made even a slight examination of familiar literature they would have found that their field of study had been thoroughly traversed.—*Journal Am. Chem. Soc.*, May, 1900.

Washington, D.C., March 20, 1900.

PRODUCTION OF OZONE BY THE DECOMPOSITION OF WATER BY MEANS OF FLUORINE.

By HENRI MOISSAN.

WHEN during any reaction the oxygen is set free at a low temperature, we observe that this simple body becomes polymerised with the greatest ease, and that ozone is formed. As an example we may mention the action of sulphuric acid on binoxide of barium or on permanganate of potash. It is true that if the reaction causes any production of heat the ozone is destroyed and we only find traces of it; by reason of the instability of ozone at the ordinary temperature its destruction may even be complete.

The action of fluorine on water furnishes a new proof of this easy polymerisation of oxygen at a low temperature.

We showed in 1891 that fluorine in the presence of water decomposes this liquid at the ordinary temperature, with the formation of hydrofluoric acid and ozone. We even remarked that by allowing a few drops of water to fall through an atmosphere of fluorine, the ozone produced was sufficiently concentrated to appear with the beautiful blue colour observed by MM. Hautefeuille and Chappuis.

We have repeated these experiments with the aid of a more abundant current of fluorine prepared in a copper vessel, and we were thus enabled to pass a large volume of fluorine through a small quantity of water.

The fluorine is passed by a small platinum tube through a water jacket kept at a constant temperature of 0°. It then passes into a Chancel flask with a round bottom, similar to those used for taking the density of gases. When this flask is filled by displacement with ozonised oxygen, this latter is titrated by means of a solution of iodide of potassium, in presence of an excess of sulphuric acid to prevent the formation of iodate. The iodine set at liberty is finally estimated by hyposulphite of sodium.

To transfer the solution of iodine into the flask without losing any ozone, a long-stemmed funnel is fixed to the central tube, and the liquid, to which sulphuric acid is added, is poured in. The flask is then thoroughly cooled down by means of carbonic acid and acetone. The gas contracts, and on opening the tap the liquid runs into the interior

* A Paper read before the Royal Society, May 31, 1900.

The solution of iodide of potassium in sulphuric acid is in this manner run in several times until the gas no longer colours the iodide.

The end of the reaction is recognised by allowing the flask to take the temperature of the laboratory and then letting a bubble of the gas pass through the tap into the funnel, in which there remains a little iodide solution. This bubble ought not to produce any colouration. After shaking, the flask is uncorked and the free iodine estimated by means of hyposulphite.

The following experiments show the regularity with which they can be carried out:—

Length of experiment.	Ozone per litre.	
	Volume.	Weight.
5 minutes	56.3 c.c.	0.1207 grm.
10 "	90.7 "	0.1945 "
30 "	143.9 "	0.3085 "

By reducing these figures to percentages we get:—

5 minutes	5.63 c.c.
10 "	9.07 "
30 "	14.39 "

According to this experiment the proportion of ozone produced in the gas was, by volume, 14.39 per cent. After this moment the quantity of ozone present remained practically constant. As the figures show, it is a fairly high proportion. In reality the concentration of the ozone produced by fluorine in contact with water is much greater than that shown by previous analyses. As a matter of fact the displacement of the air in the flask by the ozone requires a fairly long time, during which the concentrated ozone decomposes.

On the other hand, the influence of the speed of the current is very great. In our experiments the speed was 3 litres per hour. The more rapid the current of fluorine, taking care, of course, to keep the temperature down to 0°, the more concentrated will the ozone be. An equilibrium is here formed between the two following reactions:—

1. The formation of blue ozone by decomposition of the water by an excess of fluorine.
2. Destruction of the ozone by increase of the surrounding temperature.

In several series of experiments, when the speed of the current of fluorine was less than 2 litres an hour, the proportion of oxygen to ozone varied from 10 to 12 per cent. In other experiments in which the bulb containing the water was not kept cooled down to 0°, the proportion of ozone was much lower.

The easy formation of concentrated ozone by the action of fluorine on water at a temperature of 0°, may possibly become the starting point of several applications.

The preparation of fluorine by the electrolytic method is certainly a delicate operation, but it is not expensive. Further, the ozone obtained by this means does not contain a trace of oxygenated nitrogen compounds. In this method of preparing ozone all secondary reactions are prevented, and if this new method becomes in any way commercial, it will afford great evidence of the chemical activity of fluorine.—*Bull. Soc. Chim.*, Ser. 3, xxiii., No. 8.

New Work on Acetylene Gas.—Professor Vivian B. Lewes has in the press an exhaustive work on "Acetylene Gas, a Handbook for the Student and Manufacturer." The book contains over 250 illustrations, and comprises a history of acetylene, its preparation, properties, and chemical reactions, together with a complete list of legal enactments in full concerning its use and manufacture, patents, and other important data. Messrs. Archibald Constable and Co. are the publishers,

RECENT DEVELOPMENTS IN THE ACETYLENE INDUSTRY.

By M. LUNDSTRÖM.

As the result of a large number of analyses the author gives the following figures for the composition of acetylene now made from commercial carbide of calcium:—

	Minimum.	Maximum.
Sulphuretted hydrogen	0.0	1.34
Phosphoretted hydrogen	0.03	1.7
Siliciuretted hydrogen	0.0	0.8
Arseniuretted hydrogen	0.0	0.004
Ammonia	0.06	2.8
Carbonic oxide	0.0	1.48
Hydrogen	0.07	0.27
Nitrogen	0.2	2.91
Oxygen	0.55	1.18

In the event of insufficient cooling during the preparation, the acetylene may also contain benzene vapour.

In a general way commercial carbide of calcium gives a gas containing 99.5 per cent of acetylene and 0.5 per cent of other gases. The oxygen and the nitrogen come from the air enveloping the pieces of carbide. The presence of hydrogen is due to the metallic calcium formed by the dissociation of the carbide at a high temperature. The raw acetylene may even contain as much as 20 per cent of this gas.

The siliciuretted hydrogen probably comes from the silica which is always present in the lime used; as for the ammonia, it comes from the nitride of magnesium. Finally, the sulphuretted hydrogen is due to sulphide of alumina, and the phosphoretted hydrogen to phosphide of lime.

A large number of methods have been proposed for the purification of acetylene. Lunge and Cedercreutz recommend chloride of lime; Frank proposes acid solutions of metallic salts (ferric chloride or cupric chloride in hydrochloric solution); Ullmann uses an acid chromic solution; and Stern passes the gas through petroleum, alcohol, or benzene. In actual practice nearly all the impurities are absorbed by the lime-water, and a simple washing with water will even suffice, unless the gas contains a large quantity of phosphoretted hydrogen, in which case a more complete purification will be necessary. According to the author Frank's method should be preferable to any other.

Carbide of calcium and acetylene have found numerous applications besides lighting; for example, for the complete dehydration of alcohol. In this operation it is necessary to use anhydrous sulphate of copper to absorb the acetylene set free.

Acetylene can also be used for the preparation of extremely fine lamp-black. Söderbaum, again, uses it for the quantitative separation of copper from zinc, cadmium, and arsenic.

Finally, Bunsen burners have been made by means of which acetylene can be used for heating purposes.—*Chem. Gesell. Stockholm*, 1899.

NEW PREPARATIONS OF SOME OXIDES OF URANIUM.

By J. ALOY.

Uranous Oxide or Crystallised Suboxide of Uranium, UO_2 .—There are several methods of obtaining this compound:—1. Arfwedson prepared suboxide of uranium, which he took for a metal, by heating the double chloride of suboxide of uranium and potash in a current of hydrogen and removing the alkaline chloride by lavigation; 2. Wöhler obtained UO_2 in the form of a black crystalline powder, by evaporating the hydrochloric solution of uranate of ammonium and sea-salt to dryness and then

fusing; 3. A more convenient method, due to M. Ditte, consists of calcining the oxide U_3O_8 moistened with hydrofluoric acid in a platinum crucible; 4. Finally, the reduction of the oxides U_3O_8 and UO_3 by carbon, also leads to the formation of crystallised UO_2 .

To these methods the following, which is remarkably simple, may be added: to obtain the crystallised oxide, UO_2 , it suffices to heat crystallised uranic hydrate, the preparation of which is described further on, in a current of hydrogen. In this manner this hydrate is transformed into a brilliant black powder, composed of small crystals, which, examined under the microscope, appear in the form of rectangular orthorhombic plates, for the most part modified by the four angles being truncated. The uranous oxide, UO_2 , thus produced is not pyrophoric; it is even but slightly oxidisable; it must be kept for a long time at a red heat to be transformed into the green oxide. Like the other varieties of oxide, amorphous or crystallised, it is insoluble in dilute hydrochloric and sulphuric acids.

Violet Hydrate and Uranic Hydrate.—On exposing an aqueous solution of uranic oxalate to the action of the solar rays, Ebelmen observed that the solution became cloudy and deposited a flocculent material of a violet-brown colour. After being washed several times with boiling water, the precipitate no longer contained oxalic acid; Ebelmen admitted that it was an intermediate hydrated oxide, U_3O_8 . When thrown on a filter and exposed to the air until it was completely dried, this hydrate was converted into pure hydrated uranic oxide, $UO_3 \cdot H_2O$. The preparation of the violet hydrate, and consequently the hydrated uranic oxide, would thus be very simple if the low solubility of the uranic oxalate (100 parts of water dissolve 0.8 part of oxalate at 14°) did not render it impracticable.

I have tried to modify this method by using other, more soluble, salts of uranium; I was successful, more especially with the acetate. The aqueous solution of this salt is reduced by light to a certain extent; but this reaction, which is very slow, becomes, on the contrary, rapid if we cause certain organic matters to intervene, particularly alcohol or ether.

It is sufficient to expose to sunlight an aqueous solution of subacetate of uranium containing ether, to obtain a very abundant violet precipitate in a few minutes. The solution of the same salt in alcohol at 90° gives rise to an analogous phenomenon. This violet hydrate, after several washings with boiling water, no longer contains any acetic acid. It dissolves in acids giving a mixture of the uranic and uranous salts; it is therefore a hydrated uranoso-uranic oxide; it is amorphous and flocculent. I have applied the congelation method to this compound without having been able to get any definite crystalline formation, neither have I been able to obtain any satisfactory results by heating it in a sealed tube. I intend following up these experiments.

The violet hydrate, prepared by the reduction of the acetate, is less oxidisable than that of Ebelmen; it enables us, nevertheless, to obtain the pure amorphous and crystalline uranic hydrate.

Amorphous Uranic Hydrate, Crystallised Hydrate, $UO_3 \cdot H_2O$.—The uranoso-uranic hydrate is transformed with the greatest ease into uranic hydrate by oxidation in the air. It suffices to keep it moist; the uranic hydrate thus produced has the formula $UO_3 \cdot H_2O$; it is absolutely identical with that of Ebelmen. Heated to 100° with water in an open beaker, the violet hydrate oxidises and becomes crystalline. The crystals formed under these conditions belong to the orthorhombic system. When examined under the microscope they appear:—1. In rectangular orthorhombic tables, with truncations on the four angles—by suppression of the small sides some of them take a pseudo-hexagonal shape; 2. Other crystals have the appearance of rectangular orthorhombic prisms, with a principal direction of elongation. Finally, there are also observed forms in between these two types.

One of these crystals showed, in converging light, an

acute bisector perpendicular to the flat face and corresponding to $n\beta$ (negative biaxis). Following the relative values of the indices, the facets which are too small to be examined by converging light showed that their flattening was perpendicular to $n\beta$, and that the negative index (n_m) is nearer to n_g than to $n\beta$ (negative biaxis).

The formula of this hydrate is $UO_3 \cdot H_2O$. I found:—

	I.	II.	Calculated.
UO_2	88.6	88.5	88.9
Water	11.4	11.5	11.1

It is not decomposed in dry air at 100° .

M. Riban has already obtained a hydrate of the same formula, but crystallised in the hexagonal system, by heating a 2 per cent solution of subacetate of uranium to 175° , in a sealed tube, for 100 hours.—*Bull. Soc. Chim., Ser. 3, xxxiii, No. 10.*

EXPERIMENTS ON SOME NEW EXPLOSIVE AND DETONATING SUBSTANCES.

By U. ALVISI.

I PROPOSE passing in review a few new explosives which I have prepared, based on perchlorate of ammonium, and I will briefly describe the commercial production of the perchlorate.

The *cremonites*, so-called in honour of Prof. Cremona, are mixtures of perchlorate of ammonium, picric acid or picrates, and trinitrocresol or its salts. In this article I will only deal with the mixtures of picric acid and perchlorate of ammonium. The results I have obtained with these mixtures are as follows:—

1. The cavity produced in lead cylinders had the shape of an amphora.
2. The mixture of picric acid and perchlorate of ammonium, kept for more than a year, had undergone no alteration.
3. The mixtures which gave the best results had the following compositions:—

A.	{ Picric acid	2.30 parts.
	{ Perchlorate of ammonium	2.35 "
B.	{ Picrate of ammonium ..	2.46 "
	{ Perchlorate of ammonium	2.35 "

4. Numerous experiments have proved that the *cremonites* are much more powerful than picric acid alone.

5. The difference between the explosive force of picric acid and that of the *cremonites* is the more considerable as the quality of the picric acid used is inferior.

I expected, *a priori*, that mixtures of perchlorate of ammonium and coal would give rise to very powerful explosives possessing peculiar properties; and, as a matter of fact, this is the case, as I have proved in the course of my experiments. I have named these mixtures *cannel powder*, to distinguish them from ordinary powders, and to intimate that they are based on perchlorate of ammonium.

As for the kind of coal used, the boghead variety from Australia has given good results; but the best results were obtained with cannel coal from Scotia. The best mixture was composed of—

Cannel from Scotia	12 parts.
Perchlorate of ammonium	60 "

The method of making this new powder is much more simple than that of ordinary powder. The finely divided carbon is intimately mixed with the powdered perchlorate of ammonium in an apparatus to which a gyratory movement can be imparted. The mass obtained is slightly moistened with water containing a small quantity of gum; it is then compressed and granulated like ordinary

blasting powder, or made into cylinders, rods, &c., of a definite weight, and having an opening in the centre for the reception of the detonator.

When the powder is intended for use under water, it is coated with an impermeable varnish.

Samples of cannon powder kept for seven months do not show any alteration.

With regard to its uses, they are the same as those of dynamite, over which it has the advantage of being more powerful.

Commercial Manufacture of Perchlorate of Ammonium.

—The preparation of perchlorate of ammonium is based essentially on the two following facts:—

1. The transformation of chlorate of sodium into perchlorate by heat; 2. The action of nitrate of ammonium on perchlorate of sodium in concentrated solution. We obtain a precipitate formed by small crystals of perchlorate of ammonium which only require to be submitted to the drying action of the filter-pump.

Some time previous to me, in the year 1871, Th. Schloesing (*Comptes Rendus*, vol. lxxiii., p. 1271) had the idea of replacing the perchlorate of potassium with the corresponding sodic salt for the purpose of preparing perchlorate of ammonium. But this author had in no way the intention of utilising the substance obtained for the purpose of making explosive materials; his only idea, in its preparation, was to eventually derive perchloric acid from it, an analytical reagent used for the separation of sodium and potassium. But while I had recourse to nitrate of ammonium, Schloesing recommended the chloride.—*Gazzetta Chimica Italiana*, 1899, ii., p. 478.

A PRELIMINARY STUDY OF THE COBALTICYANIDES.*

By E. H. MILLER and J. A. MATHEWS.

SEVERAL years ago, during the course of an investigation of the ferrocyanides of zinc and manganese (*Fourn. Am. Chem. Soc.*, 1897, xix., 547), it was suggested that a study of the reactions between potassium cobalticyanide and solutions of metallic salts might be of interest, and that possibly this compound might be found useful as a reagent in either qualitative or quantitative analysis. A careful search through the literature showed that the subject had not been thoroughly investigated; that the cobalticyanides of many metals were unknown, and that the properties, especially the solubilities, of the known cobalticyanides, were but incompletely recorded. Apparently no work has been done on these compounds for many years, while most of the investigations bear dates prior to 1857.

The general procedure adopted in this work was:—

First.—To try the action of a half-normal solution of potassium cobalticyanide (based on the hydrogen equivalent in grms. per litre) on half-normal solutions of all the common metals. They were first added to each other in equal quantities and the filtrate tested to see which reagent was in excess; and, having found the amount of potassium cobalticyanide needed to precipitate a given metal, to work in subsequent experiments with quantities which gave a slight excess of the precipitant. Although these solutions were only approximately half-normal, they were made with sufficient care to distinguish in the resulting precipitates between a normal cobalticyanide and a double potassium-metallic cobalticyanide. The indications show that in nearly every case a normal salt is produced by a reaction of simple double decomposition.

Second.—The solubility of the precipitates so obtained was tested in every instance in nitric, hydrochloric, sul-

phuric, acetic, and oxalic acids, in ammonium hydroxide and caustic potash; in all cases both cold and hot.

These tests were made by adding the acid or alkali to the original liquid containing the precipitate, and, in each instance, an amount of solvent equal in volume to the original liquid was employed. A few precipitates were filtered, and their solubilities tested in concentrated acids.

The special solutions used were of the following strengths:—

$K_3Co(CN)_6$ (N/2)	55.52 grms. per litre.	
HNO_3 (1 : 3)		sp. gr. 1.135 = 22 per cent
HCl (1 : 1)		" 1.10 = 20 "
H_2SO_4 (1 : 4)		" 1.20 = 28 "
$HC_2H_3O_2$		" 1.03 = 22 "
$H_2C_2O_4$ (saturated solution)		" = 10 ± "
NH_4OH (1 : 2)		" 0.96 = 10 " NH_3
KOH		" 1.11 = 10 " K_2O

No highly coloured or characteristic precipitates have as yet been found which can be employed as indicators to show an excess of potassium cobalticyanide, nor do the precipitates settle readily enough to allow this point to be determined by cautious additions of cobalticyanide to the clear supernatant liquid or by spot tests. In every precipitation the potassium cobalticyanide was added to the metallic salt solution and the presence of either substance in excess had usually to be determined in a few drops of the filtrate from the resulting precipitate. The experimental part of our work will show that, in general, the cobalticyanides insoluble in water, are also insoluble in and unaffected by acids, but are soluble in or decomposed by alkalis. None of them are decomposed by boiling, as is the case with several ferricyanides. There is little similarity in either solubility or appearance between the corresponding ferri- and cobalticyanides. The metals, except those of the alkalis and alkaline earths, were taken up in their qualitative sequence, beginning with the silver-lead-mercury group.

Silver Cobalticyanide.—When equal volumes of half-normal silver nitrate and potassium cobalticyanide solutions are mixed, the silver is completely precipitated as silver cobalticyanide, a white curdy precipitate, which settles and filters well; is insoluble in all the acids used, being transposed by hydrochloric acid; is soluble in ammonia, and decomposed by potassium hydroxide giving a precipitate consisting mostly of silver oxide.

Lead Cobalticyanide.—Neither lead acetate nor nitrate are precipitated by potassium cobalticyanide, either in neutral or acid solutions. Zwenger (*Liebig's Ann. Chem.*, lixii., 158) made it from lead carbonate and cobalticyanhydric acid. This salt, crystallising in laminated crystals containing 4 molecules of water, he says, is soluble in about three parts of water, from which solution it is precipitated by ammonia as a basic salt.

Mercurous Cobalticyanide.—Mercurous nitrate gives with potassium cobalticyanide a white flocculent precipitate, which settles quickly. It was therefore possible to use concentrated ammonia as an indicator. Spot tests on porcelain showed a black precipitate as long as there was an excess of mercurous nitrate. Mercurous cobalticyanide is transposed by hydrochloric acid, and seems to be partly changed by hot sulphuric acid, but not by oxalic acid. It is unaffected by nitric and acetic acids, but decomposed by alkalis. Mercurous cobalticyanide is probably a normal salt having the formula $Hg_2Co(CN)_6$.

Mercuric Cobalticyanide is unknown. There is no precipitate formed when potassium cobalticyanide is added to mercuric chloride either in neutral or acid solution.

Arsenic, in hydrochloric, sulphuric, or ammoniacal solution gives no precipitate.

Antimony, in a solution sufficiently acid to prevent the precipitation of a basic salt, gives no precipitate.

Stannous salts in neutral, acid, or potassium hydroxide solution are not precipitated by potassium cobalticyanide. Gmelin (*"Handbook of Chemistry,"* 1852, vol. vii., p. 495) states that stannous but not stannic salts are precipitated,

* Contributions from the Havemeyer Laboratories, Columbia University. From the *Journal of the American Chemical Society*, vol. xxii., No. 2.

SOLUBILITIES OF THE COBALTCYANIDES.

$K_3Co(CN)_6$	(1). HNO_3	(2). HCl.	(3). H_2SO_4	(4). $H_2C_2H_3O_3$	(5). $H_2C_2O_4$	(6). NH_4OH	(7). KOH.	Remarks.
+ $AgNO_3$, white curdy precipitate	(cold) $\frac{1}{2}$ (hot) $\frac{1}{2}$	$AgCl$ $AgCl$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	Partly s s	Ag_2O Ag_2O	Precipitation complete. Settles and filters well. (6) White crystalline precipitate (double salt) on evaporation. Easily soluble cold concentrated $NH_4(OH)$.
+ $Hg_2(NO_3)_2$, white flocculent precipitate	$\frac{1}{2}$ $\frac{1}{2}$	Hg_2Cl_2 Hg_2Cl_2	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$NH_2Hg_2NO_3$ $NH_2Hg_2NO_3$	Hg_2O Hg_2O	(3) Seems slightly soluble hot or else is partly changed to Hg_2SO_4 . (5) Not changed to oxalate.
+ $CuSO_4$, turquoise-blue precipitate	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	s s	CuO CuO	Filters well. (6) Intense blue solution, giving double NH_3 compound on evaporation. (7) Turns green, getting darker until black CuO separates.
+ $Bi(NO_3)_3$, dense white precipitate	$\frac{1}{2}$ $\frac{1}{2}$	Easily s s	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$Bi(OH)_3$ Bi_2O_3	Precipitation done in strongly acid solution to prevent basic salts upon dilution. (6) Not transposed to $Bi(OH)_3$.
+ $CdCl_2$, white amorphous precipitate	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ s	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	s s	$Cd(OH)_2$ $Cd(OH)_2$	Filters badly. (2) precipitates again on cooling.
+ $FeCl_6$, green, becoming yellow	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$Fe_2(OH)_6$ $Fe_2(OH)_6$	$Fe_2(OH)_6$ $Fe_2(OH)_6$	(5) When freshly precipitated and greenish it is readily soluble in oxalic acid. Ammonia salts in quantity prevent precipitation and excess of $K_3Co(CN)_6$ retards it.
+ $FeSO_4$, faintly yellowish white precipitate	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	Partly $Fe(OH)_2$ $Fe(OH)_2$	$Fe(OH)_2$ $Fe(OH)_2$	(1, 2, and 3) On boiling oxidises more or less to yellow ferric cobalticyanide. (6 and 7) Some oxidation to dark coloured ferrous-ferric compounds.
+ $MnCl_2$, white precipitate	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$Mn(OH)_2$ and $Mn_2O_2(OH)_2$	$Mn(OH)_2$ and $Mn_2O_2(OH)_2$	(1, 2, 3, 4, and 5) Seem very slightly soluble hot.
+ $ZnSO_4$, dense white precipitate	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	Easily s s	Easily s s	(4 and 5) Bump violently on boiling.
+ $CoCl_2$, rose pink precipitate	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	Partly s Partly s	$Co(OH)_2$ $Co(OH)_2$	(6) Solubility increased by ammonium salts. Almost completely soluble in hot concentrated NH_4OH . (7) At first blue basic salts, turning again pink.
+ $NiCl_2$, robin's egg blue precipitate	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	Blue sol. s s	$Ni(OH)_2$ $Ni(OH)_2$	Very voluminous precipitate, which filters poorly.
$NH_4Li, Na, Mg, Ba, Ca, Sr, Pb, Hg, Sn^{++}, Cr, Al, Pt, Au, Zr, Ti, Mo$ salts						No precipitates.		Solutions of salts of other metals are not precipitated by $K_3Co(CN)_6$ and other known cobalticyanides are easily soluble in water. Such cobalticyanides are usually made from an oxide or hydroxide acted upon by $H_3Co(CN)_6$.

but does not give the conditions under which he obtained the precipitation.

Cupric Cobalticyanide.—When a solution of copper sulphate is completely precipitated by potassium cobalticyanide solution, there results a turquoise-blue compound. This salt, apparently $\text{Cu}_3\text{Co}_2(\text{CN})_{12}$, is insoluble in all acids, cold or hot; very soluble in ammonia, and with caustic potash it turns green, becoming darker and darker until black cupric oxide separates. The ammoniacal solution upon evaporation gives small shining blue crystals, to which Zwenger (*loc. cit.*), who first worked with this compound, assigns the formula $\text{Cu}_3\text{Co}_2(\text{CN})_{12} \cdot 2\text{NH}_3 \cdot 5\text{H}_2\text{O}$.

Cuprous Cobalticyanide, of which no mention is found in the literature, results from the precipitation of cuprous chloride by means of potassium cobalticyanide. It is a faintly yellow precipitate, which filters badly; it is insoluble in acids and cold ammonia, but soluble in hot dilute ammonia. It is partly decomposed by potassium hydroxide in the cold, and completely when hot. It is slowly oxidised by nitric acid, giving the blue cupric cobalticyanide.

Bismuth Cobalticyanide.—A solution of bismuth nitrate, rather strongly acid with nitric acid, is precipitated by potassium cobalticyanide, giving a dense white precipitate, very soluble in hydrochloric but insoluble in the other acids and ammonia. Potassium hydroxide gives in the cold $\text{Bi}(\text{OH})_3$, which, on boiling, may be changed to yellow Bi_2O_3 . The original precipitate seems to be a normal cobalticyanide, but it has not yet been analysed, and no mention of such a compound was found in the literature.

Cadmium Cobalticyanide.—The statement appears in Gmelin's "Chemistry" (1852), that with cadmium sulphate, potassium cobalticyanide forms a brown precipitate, turning white later, soluble in excess of cobalticyanide and also in acids. In our experiments cadmium chloride was employed; the precipitate was white and amorphous, not soluble in excess of cobalticyanide, nor in any acid except warm hydrochloric acid, from which it re-precipitates on cooling. To determine whether it is changed or not during this treatment will require quantitative work. It is completely soluble in cold ammonia, but potassium hydroxide decomposes it, giving cadmium hydroxide.

Solutions of gold, platinum, titanium, vanadium, uranium, or zirconium are not precipitated by potassium cobalticyanide.

Aluminum chloride and chromium salts gave no precipitate with cobalticyanide. Certain double ammoniochromic cobalticyanides have been described by Christensen (*Y. Prakt. Chem.* [2], xxiii., p. 52) and by Braun (*Liebig's Ann. Chem.*, cxxv., 153, *et seq.*).

Ferric Cobalticyanide.—When potassium cobalticyanide is added to a solution of ferric chloride, no precipitate forms at first, but the solution assumes a light green tint, and on standing a few minutes becomes cloudy and iridescent. The precipitation increases with the formation of an amorphous yellow precipitate which runs through the filter. By boiling, it becomes canary-yellow and flocculent, filtering fairly well. The precipitation does not seem to be complete; it is retarded by the presence of an excess of cobalticyanide or by large quantities of ammonium salts. The precipitate once formed is not soluble in cobalticyanide solution, nor in mineral acids, cold or hot, dilute or concentrated. Hydrochloric acid changes the colour of the precipitate, and renders it almost impossible to filter. Insoluble in acetic acid, cold or hot; when freshly precipitated it is instantly soluble in oxalic acid, but re-precipitates on boiling. It seems that at least two different compounds are produced; they differ both in colour and solubility; the greenish one is soluble in oxalic acid, and the yellow one insoluble. The latter is formed by long standing in the cold, or rapidly by heating. Both give ferric hydroxide with ammonia or potassium hydroxide in the cold. If the ferric salt and the cobalticyanide solutions are mixed hot, precipitation of the yellow compound is instantaneous, no matter which

reagent is in excess. The well-washed ferric cobalticyanide gives no red colour with ammonium thiocyanate.

Ferrous Cobalticyanide.—Ferrous sulphate and potassium cobalticyanide seem to give a normal ferrous cobalticyanide, a slightly yellow, amorphous, slow-settling precipitate. When an excess of cobalticyanide is present there is no oxidation or change of colour in the ferrous cobalticyanide, even upon long boiling. The precipitation is complete and filters well. With nitric acid, cold and hot, and with hydrochloric and sulphuric acids, hot, there is oxidation. The precipitate darkens in varying degrees, most with nitric and least with sulphuric acid. After treatment with these acids the precipitate filters badly. No change is noticed with acetic or oxalic acids; in the presence of the latter it filters very well. With ammonia the precipitate is partially decomposed in the cold, becoming bluish, and by boiling is completely converted into ferrous hydroxide. With potassium hydroxide it gives a greenish tint, darkening on standing, becoming slate-coloured by boiling, forming probably a mixture of ferrous and ferroso-ferric hydroxides.

Manganese Cobalticyanide.—This precipitate, apparently normal, is pure white and filters well. It is insoluble in all cold acids, but not absolutely so in hot mineral acids. Alkalis decompose it, giving first $\text{Mn}(\text{OH})_2$, and later, by oxidation, $\text{Mn}_2\text{O}_2(\text{OH})_2$.

Zinc Cobalticyanide is formed when a solution of zinc sulphate is precipitated by potassium cobalticyanide. It is pure white, settles quickly, and filters well; insoluble in hot water, cold or hot acids, except that a trace seems to dissolve in hot sulphuric acid. This precipitate as well as a few others, *e.g.*, ferrous and ferric cobalticyanides, on boiling with hydrochloric acid passes into a condition which renders it impossible to filter even on double filters. It is very soluble in alkalis.

Cobalt Cobalticyanide.—From solutions of cobaltous chloride, potassium cobalticyanide precipitates a rose-pink, amorphous, rather gelatinous precipitate which is insoluble in cold and hot acids. At 100° , or even lower, it loses water and becomes blue. This fact was noted by Zwenger, who also states that he formed this compound by heating cobalticyanhydric acid with concentrated sulphuric acid and diluting with water before the decomposition was complete. A peculiarity of many cobalticyanides is the large amount of water which they retain after drying at 100°C . Zwenger noticed that the blue anhydrous cobaltous-cobalticyanide rapidly absorbs moisture from the air, and that when water is poured upon it there is a considerable evolution of heat. We found that the ferrocyanides of zinc and manganese acted in the same way. When cobaltous cobalticyanide is treated cold with ammonia, it gives a brown solution and pink residue; on boiling, the solution becomes pink and the residue greenish-brown. The presence of ammonium salts increases the solubility of this compound in ammonia; it is completely soluble in concentrated ammonia. Caustic potash gives first blue basic salts, and on standing or boiling rose-coloured cobaltous hydroxide.

Nickel Cobalticyanide results when potassium cobalticyanide is added to solutions of nickel salts. Zwenger states that this precipitate cannot be washed free from potassium salts, and that the pure nickel cobalticyanide, $\text{Ni}_3\text{Co}_2(\text{CN})_{12}$, must be made from cobalticyanhydric acid and a nickel salt. The precipitate is robin's egg blue in colour, very voluminous, and dries up to a vitreous mass with conchoidal fracture. It is insoluble in water and acids, cold or hot; soluble completely in ammonia, cold or hot. Potassium hydroxide gives instantly pale green nickel hydroxide.

The effect of the reagents used on the precipitates formed by potassium cobalticyanide is shown by the accompanying table. A glance at this tabulation will show several possibilities for new separations:—

1. The lead salt is exceedingly soluble, while those of silver, copper, and bismuth are insoluble in either water

or nitric acid. This may find an application in the analysis of pig lead, when the separation of relatively small quantities of these impurities would be much more preferable to the separation of the lead as sulphate. The separation of the bismuth can be effected either by treatment with hydrochloric acid, which dissolves the bismuth cobalticyanide and leaves the copper as cobalticyanide and the silver as chloride, or by ammonia which leaves the bismuth and dissolves the copper and silver. The bismuth compound, if not suitable for weighing, can be decomposed by potassium hydroxide and weighed as Bi_2O_3 , or one of the new volumetric methods may be employed for its estimation.

2. As the precipitation of ferric cobalticyanide in the cold can be completely prevented by the presence of ammonium sulphate, and probably by other compounds, it is possible to precipitate zinc, manganese, nickel, or cobalt in the presence of iron. With zinc ores containing iron and manganese, the manganese and zinc can be precipitated as cobalticyanides, and then separated by treatment with potassium hydroxide, which readily dissolves the zinc cobalticyanide and leaves the manganese as $\text{Mn}_2\text{O}_2(\text{OH})_2$.

Another possible application is in the analysis of nickel steel, where the separation from ferric iron, if sufficiently complete, would be more convenient than the method in use, based on the solubility of ferric chloride in ether. The nickel cobalticyanide after filtration can be converted into hydroxide and then dissolved in acid for the cyanide titration or for electrolysis.

These and other possible uses of the cobalticyanides are under investigation at Columbia University.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 8th, 1900.

Dr. J. H. GLADSTONE, F.R.S., Vice-President, in the Chair.

A PAPER ON "The Magnetic Properties of Alloys of Iron and Aluminium" (Part II.), by S. W. RICHARDSON and L. LOWNDS, was read by Dr. RICHARDSON.

Experiments have been made to ascertain in what way the hysteresis loss between given limits of the field strength is connected with the temperature for an alloy containing 3.64 per cent of aluminium. The experiments show that the hysteresis loss attains a maximum value at a temperature considerably higher than the temperature of maximum induction. The changes produced in the magnetic properties of the alloy by heating and subsequent cooling have also been investigated. The properties depend largely on the previous history of the specimen, but there does not appear to be any essential difference between the behaviour of the alloy during heating and cooling (except near the temperature of minimum permeability). Experiments have also been conducted on the abrupt change in the permeability that takes place at a temperature of about 650°C . The conclusions arrived at are as follows:—(1). The hysteresis loss at first diminishes as the temperature rises. It then increases, and reaches a maximum at about 550°C . On further heating it falls off rapidly, and is negligible at 700°C . (2). The magnetic properties of the specimen depend largely on its previous history. (3). There is no essential difference between the behaviour during heating and cooling except near the temperature of minimum permeability. (4). An abrupt increase in the permeability takes place at about 650°C . during heating, followed by an equally abrupt diminution on further heating. (5). This abrupt change is more marked with falling than with rising temperatures. (6). Continued heating and cooling diminish

the permeability. (7). The curve connecting temperature of minimum permeability and percentage of aluminium is a straight line. (8). The microscopic examination of the specimens shows the presence of crystals.

Prof. S. P. THOMPSON asked if the specimens had been kept for any length of time at a high temperature, because crystals changed and grew in metals at temperatures even far below their melting-points.

Prof. REINOLD asked if any specimens had been examined where the crystalline structure had not been observed.

Mr. BLAKESLEY asked if any explanation of the orientation of the crystals could be given.

The CHAIRMAN said it was difficult to know exactly what substances were being dealt with. They might be pure alloys, or mixtures of two or three alloys with iron or aluminium.

Dr. RICHARDSON, in reply, said the crystals might be dissolved in nitric acid and analysed, but at present he did not know their composition.

Mr. W. CAMPBELL then read a "Note on Crystallisation produced in Solid Metal by Pressure."

In the preparation of sections of tin, particles cling to the file, and, if allowed to remain, tend to tear the surface of the metal. The effect is not immediately noticeable, but on etching the polished surface there appear, besides the usual structure of the tin, lines of much smaller crystals with irregular boundaries, but possessing different orientation. The effect is only superficial because it can be removed by polishing. The same behaviour is noticed in some alloys, and it would thus appear that the pressure of a file is sufficient to cause a metal or an alloy to rearrange itself.

Prof. S. P. THOMPSON suggested that the effect might be due to local heating caused by tearing rather than to pressure.

Mr. CAMPBELL said the effect was not due to the heating of the file, because if the file were kept perfectly clean no crystals formed.

Prof. S. P. THOMPSON asked if scratching the surface with a diamond produced crystallisation.

The author said he had tried with a sharp knife without success, but cutting with a blunt chisel produced crystallisation along the chisel mark.

A paper on "The Viscosities of Mixtures of Liquids and Solutions" was read by Dr. C. H. LEES.

Three formulæ have been suggested for expressing the viscosity of a mixture in terms of the percentages and viscosities of its constituent parts. The first of these represents the viscosity as being the sum of a number of terms, each one of which is the product of the percentage of any constituent and its viscosity. The second formula represents the logarithm of the viscosity in a similar manner, and the third one the reciprocal. None of these formulæ represent the viscosity of a mixture with closeness. The author suggests a formula in which the m th power of the reciprocal of the viscosity of a mixture is equal to the sum of a number of terms, each one of which is the product of the percentage of any constituent, and the m th power of the reciprocal of the viscosity of that constituent. This formula gives satisfactory agreement, and moreover leads to Slotte's formula for the variation of viscosity with temperature.

The SECRETARY read a note from Prof. WOOD on "An Application of the Method of Stria to the Illumination of Objects under the Microscope."

The object chosen was powdered glass immersed in cedar oil of the same refractive index. The glass particles were almost invisible under ordinary conditions of illumination. The illuminating system was then arranged as follows:—A screen bounded by a straight edge was placed in front of an incandescent gas lamp so as to cut off half of the mantle, and give a source of light bounded by one perfectly straight edge. A small lens of very short focus was placed below the stage as close as possible to the

object. The lamp was at a distance of six feet, and the light reflected from the mirror was brought to a focus by this lens, passing through the object on its way. An image of the lamp was formed in space and viewed by the microscope. A little strip of thin brass with a carefully cut straight edge was fastened to the stand carrying the bull's-eye condenser, and moved into position between the objective and object, so as to cut off the flame image with the exception of a narrow thread of light along the straight edge. The brass screen must be in the plane of the flame image with its edge parallel to the straight edge of the flame. The brass was then advanced over the flame until nearly all the light was cut off. Upon lowering the microscope until the object was in focus, and carefully advancing the brass strip until practically all the flame image was cut off, it was found that the glass particles suddenly appeared with great sharpness, showing as distinctly as if in air. Two photographs of glass in oil were shown, one taken with ordinary illumination, and the other by the Schlieren-Methode.

The meeting then adjourned until June 22nd.

ROYAL INSTITUTION.

General Monthly Meeting, June 11th, 1900.

Sir JAMES CRICHTON-BROWNE, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE following were elected Members:—Mr. C. E. Baxter, Mr. C. Coward, Mr. A. Dupré, Mr. L. V. Harcourt, Mr. W. C. Prescott, and Mrs. M. F. Thorne.

The special thanks of the Members were returned to Mr. Harold Swithinbank for his donation of £50 to the fund for the Promotion of Experimental Research at Low Temperatures.

The Managers reported, that at their meeting held this day the following Resolution was unanimously agreed to:—

"The Managers of the Royal Institution of Great Britain, on the occasion of the retirement of Sir Frederick Bramwell from the office of Honorary Secretary, desire to place on permanent record an expression of their high appreciation of the admirable way in which he has performed the duties of that office and of his signal services to the Institution generally.

"Elected a Member of the Royal Institution in 1876, Sir Frederick Bramwell has since then delivered seven Friday Evening Discourses on subjects cognate to that branch of applied science with the progress of which in this country, during the Victorian Era, his name must ever remain honourably associated.

"Having joined the Board of Managers in 1879, he was induced, in 1885, notwithstanding professional engagements of the most onerous and responsible character, to undertake the additional burden of the duties of Honorary Secretary to the Institution. For fifteen years these duties have absorbed no inconsiderable proportion of his time, and have been discharged with incomparable energy, business ability, and courtesy. Himself a generous patron of the Institution, and foremost to support every project for its advantage, he has been able to suggest improvements in the administration of its property which have added to its material resources. Mainly concerned in the arrangement of the courses of Lectures and Friday Evening Discourses, he has succeeded with no small expenditure of labour in maintaining these at a high level of educational value, and in making them attractive and popular and representative of every modern advancement in the arts and sciences. While extending the usefulness of the Institution in every direction, and introducing into it many new members, he has by his genial personality done much to promote smoothness and harmony of working in its several departments.

"The Managers feel that the Royal Institution has been singularly fortunate in having so long enjoyed the services of Sir Frederick Bramwell in the capacity of Honorary Secretary, and they rejoice to know that although he is no longer to fill that office, they are still to have the benefit of his counsels at their Board. Sir Frederick Bramwell's name is indelibly stamped upon the history of the Royal Institution for the last quarter of the nineteenth century. He will always be gratefully remembered by its Members, but the Managers wish to add to personal remembrance this formal record of their cordial recognition of his merits."

The CHAIRMAN announced that a desire had been expressed that a bust of Sir F. Bramwell should be placed in the Royal Institution.

NOTICES OF BOOKS.

Richter's Organic Chemistry, or Chemistry of the Carbon Compounds. Edited by Prof. R. ANSCHÜTZ. Authorised translation by EDGAR F. SMITH, Professor of Chemistry University of Pennsylvania; third American from the eighth German Edition. Vol. II. *Carbocyclic and Heterocyclic Series.* With illustrations. London: Kegan Paul, Trench, Trübner, and Co., Limited. 1900. Pp. 671.

The first volume of this work was noticed in this column on March 2, 1900, and in a general sense we have nothing to add to the remarks we then made in regard to the general excellence of the book.

Volume II. deals with the compounds of the carbocyclic and the heterocyclic series. The first of the above series comprises the tri-, tetra-, penta-, and heptacarbo-cyclic compounds, which are disposed of in a few pages; these are followed by the large and important group of hexa-carbo-cyclic compounds, to which considerably more than half the volume is devoted. We next come to Part III. on the heterocyclic compounds, comprising the three, four, five, and six numbered heterocyclic substances.

In our notice of Vol. I. we referred to the excellent index of 36 pages; Vol. II. is even better equipped in this respect, the index consisting of no less than 65 pages of two columns each, which, we read, is due to the patient work of Messrs. W. Taggart, O. L. Shinn, and J. B. Moyer.

Field Testing for Gold and Silver. By WM. HAMILTON MERRITT, F.G.S., &c. London: Crosby Lockwood and Son. 1900. Pp. 144.

As a practical man the author soon found that the elaborate blowpipe sets prepared for colleges were much too complicated for the field, and in this practical manual for miners and prospectors he has shown how good results can be obtained with very cheap and simple appliances.

Field testing takes up about half the pages of this book, and comprises all the necessary instructions for sampling, panning, the use of the blowpipe, ivory-scale, and more complete assays with the field furnace. The second part deals with practical mineralogy, geology, and the diagnostic characters of rocks. Part III. contains a glossary of useful mining terms. We must, however, warn our readers against a too free use of such terms; they are often used to disguise ignorance, and will frequently deceive the unwary investor, who is apt to think that a man using such an excess of technical language must necessarily have had great experience.

This pocket-book is of a convenient size, well bound, and illustrated with nine plates from photographs, and numerous figures in the text.

A Pocket-book for Chemists, Chemical Manufacturers, Metallurgists, Dyers, Distillers, Brewers, Sugar Refiners, &c. By THOMAS BAYLEY, Assoc. R.C.Sc.I. Seventh Edition. Revised and enlarged. London: E. and F. N. Spon, Limited; New York: Spon and Chamberlain. 1900. Pp. 559.

BAYLEY'S Chemists' Pocket-book is so well known that it needs but few words to remind our readers of its excellent character. The present edition has been re-arranged, and to a great extent re-written, and shows a marked contrast to the first edition, published in 1878, which consisted of 421 pages only. This pocket-book is without doubt the best of its kind, and we hope the author will be as successful in the future as he has been in the past.

Arithmetical Exercises in Chemistry. By LEONARD DOBBIN, Ph.D. With a Preface by Professor CRUM BROWN. Third Edition. Edinburgh: James Thin; London: Simpkin, Marshall, and Co., Limited. 1899. Pp. 52.

THE usefulness of this book may be gauged by the fact that a third edition is now required. The general plan of the work remains unaltered, but the opportunity has been taken to introduce, in the form of appendices, the Denominations of the New Metric Standards, and the Tables of Imperial and Metric Equivalents adopted by the Board of Trade, and approved by orders in Council, May 19, 1899. A few other changes have been made, and additional exercises included.

The Arithmetic of Chemistry. By JOHN WADDELL, B.Sc. (Lond.), Ph.D. (Heid.), D.Sc. (Edin.). London and New York: Macmillan and Co., Limited. 1899. Pp. 133.

IN these pages the author gives a simple treatment of chemical calculations with a view to smoothing away the difficulties encountered by students in this direction. In preparing for examinations, as well as in studying chemistry with a view to retaining knowledge, students will obtain great assistance from this book, as the points dealt with are very clearly expressed; in this connection we may mention the manner in which the author puts forward the grm.-molecular volume of gases, a subject which has been a stumbling block to many beginners.

The Splitting-up and the Properties of Phenylglycolic Acid.—E. Rimbach.—Phenylglycolic acid has been split up by M. Dewkowitsch; according to the author, the following are the best conditions for effecting this decomposition:—60 parts of the acid, and 120 parts of crystallised cinchonine are dissolved in 3 litres of water, and heated for an hour on the water-bath; then, after standing for twelve hours, it is filtered and crystallisation started by dissolving a certain quantity of chloride of sodium in the liquid. In this manner about 100 parts of the right-handed salt are obtained; this is purified by crystallisation in boiling water. Right-handed phenylglycolic acid crystallises in hemimorphous clinorhombic prisms. Its rotatory power in aqueous solutions increases considerably with dilution (143.7° for 0.058 per cent). Its rotatory dispersion is normal and fairly strong. Inactive synthetic phenylglycolic acid constitutes a racemic, and not a mixture. The left-handed phenylglycolate of cinchonine which remains in the mother-liquor crystallises in hemihedral rhombic tables. Its rotatory power in aqueous solution (at 2.33 per cent), is $[\alpha]_D = +92.1^\circ$; that of the right-handed salt is $[\alpha]_D = +152.4^\circ$, for a concentration of 2.43 per cent. The author has determined the solubilities in water of the two salts, and of the right-handed acid at different temperatures.—*Berichte*, xxxii., p. 2385.

CORRESPONDENCE.

THE ADVANTAGES OF UNIFORMITY IN MANURE ANALYSIS.

To the Editor of the Chemical News.

SIR,—Referring to the letter from one of us re "Uniformity of Chemical Manure Analysis" (CHEMICAL NEWS, vol. lxxxi., p. 143), it might be interesting and instructive to point out the advantages that would result from that uniformity for all interested parties.

As was already shown, there would be an enormous advantage for the manufacturer. As things are at present, there is constant cause for disagreement by discrepancies, rude surprises by too low tests, &c.; and the chemical analysis, instead of being a trustworthy guide for him, will very often only confuse him. Say, for instance, a public chemist gives a totally different analysis of a sample than his own works official had certified. To make sure of the test, he sends the sample to a third chemist, with the result that perhaps he has to choose now between three different results; or, say, he believes the test of the second chemist, which may show too low, and alters his mixing according to his test; he may find that the next sample from this altered mixing, tested by another referee chemist, would show a result far too high, thereby showing great waste in materials if he has to take this latter test as being correct.

Such things could never occur if uniformity of methods would be introduced; the chemical analysis would then be a really true guide for the manufacturer. One chemist would find the sample to be much the same as another, if their separate analyses were correctly performed. If a manufacturer wants to deliver a really good article, he knows exactly how to regulate his mixings accordingly, and need—as at present he has—have no fear of finding his manures condemned as being below guarantee, simply by the discrepancies due to want of uniformity.

On the other hand, those less scrupulous manufacturers who purposely try to take advantage of the confusion caused by the very varying analyses furnished by different chemists, would soon have their sharp practice brought to light and effectually stopped.

And this is where the farmer would greatly benefit. It is to his interest, chiefly, that the manure trade should be firmly fixed on fair and honest lines; and that he can have an absolutely sure guide, through the analysis, for finding the fair dealing firms, and thus protect himself against would-be fraudulent dealers.

With more confidence he will then see in the public chemist his indispensable never-failing adviser, and more than ever will he seek his advice; there will be more work for the public chemists instead of less, as some of them may fear, and the public generally will have a much higher opinion of the profession than possibly it may have at present. Now it may often be heard in industrial circles of a "buyer's" chemist and a "seller's" chemist, in that sense that the first is thought to try to favour the buyers by his relatively low, the latter the sellers by his relatively high, results. For the sake of the honour of the analytical chemists of Great Britain and Ireland, we are much inclined to attribute these divergent results, in nearly every case, to the want of uniformity, and only in exceptional ones to direct and intentional fraud. Knowing as we do the different results arrived at by different methods, and knowing also that most probably a chemist keeps to a method once it has found favour in his sight, may explain partly why certain members of the profession are frequented by "buyers" and others chiefly by "sellers," because these two soon find out the one who, in their eyes, gives the best results.

If, then, uniformity was introduced, such terms as mentioned above would be speedily dropped, assuming of course that it is the want of uniformity from which such

things spring; and, on the other hand, if there were any impure intentions on the chemists' part, they also would be most effectually checked, as a too high or too low result could then be very easily proved to be incorrect.

As regards the works' chemist, each will know himself well enough how much bother, annoyance, useless work, and waste of time uniformity would save him. The manufacturers and managers are only too much inclined to make their works' chemists responsible for discrepancies, and indeed it is only natural, if these appear over and over again; and yet even the greatest care and over-anxious accuracy on the part of the works' chemist cannot help it, if the real source is not removed.—that is, want of uniformity.

Therefore *Uniformity in the Methods of Chemical Manure Analysis* would be highly beneficial to all parties concerned. Still, in spite of this, nothing has been done in the matter of this great reform, though there is, to our mind, more than one way possible.

The greatest and most widely-reaching help, of course, would come if the government took the matter into their own hands. If that were impossible, the public chemists have sufficient power to bring about this desirable reform by agreeing amongst themselves upon some certain fixed method for analysis of manures, and making that method rigidly official. If that were done, we have not the slightest doubt but that it would soon be adopted by the manufacturers; and the opportunity also arises for the manufacturers to set the ball of reform in this matter rolling, if the bigger firms adopted any particular method and only bought and sold on the results furnished by that method.

In Germany the matter has been settled by the "Control und Versuchsstationen," and in other European states, also in the United States, arrangements of one kind or another have been made. Why, then, should the United Kingdom be left behind in the endeavour to make this most important branch of chemical manufacture as near perfection as possible.

A. YOUNG.
W. JERWITZ, Ph.D.

Dublin, June 6, 1900.

SYNTHESIS OF ARSENIC.

To the Editor of the Chemical News.

SIR,—The remarks of "Analyst" in criticism of my note that "there is evidently an error in the figures" given by Prof. Fittica, are not justifiable. If 0.501 grm. phosphorus yields 0.2012 grm. arsenic sulphide, the percentage of arsenic would be 24.4, and not 2.5 as stated in the German original. The figures, therefore, are not "perfectly correct."—I am, &c.,

THE TRANSLATOR.

June 9, 1900.

SYNTHESIS OF ARSENIC.

To the Editor of the Chemical News.

SIR,—In reply to "Analyst's" letter of June 8th, I would beg to point out, what I should have thought would have been evident to most readers, that "there is evidently an error in these figures." If 0.501 phosphorus is equivalent to 0.2012 As_2S_3 , then the percentage of As is 24.49, and not 2.5 as given in the paper, thus confirming the translator's remark.—I am, &c.,

ANOTHER ANALYST.

London, S.W., June 9, 1900.

DISTILLATION WITHOUT BUMPING.

To the Editor of the Chemical News.

SIR,—May I inform the gentleman who has written to you re the above, and whose letter was published in CHEMICAL

NEWS, vol. lxxxii., p. 263, that the device he mentions was well known to alchemists when I was on the earth.—I am, &c.,

A GHOST OF 200 YEARS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 20, May 14, 1900.

Hydrated Peroxides of Calcium.—M. de Forcrand.—Mixtures of solutions of hydrogen peroxide and the base show that lime forms, like baryta and strontia, precipitates of hydrated peroxide more soluble than those of the peroxides of strontium, but less soluble than the corresponding barium salts. Between 10° and 16° baryta and strontia give precipitates containing 8 or 9 molecules of water, whilst the calcium precipitate contains only 2 molecules of water, and has a very different heat of formation. The transformation of calcium dioxide into the hydrated state depends solely on the temperature; the critical temperature being somewhere about 15–20°.

Allotropic Transformation of Alloys of Iron and Nickel.—L. Dumas.—Dewar and Fleming showed that when an alloy of nickel and iron containing 29.07 per cent of nickel is immersed in liquid air, a non-reversible transformation takes place. This particular alloy begins to undergo the reversible transformation above 0°. Carbon has the property of lowering the point of non-reversible transformation. The author continues the study of this alloy, and finds that nickel lowers the points of transformation of iron, and iron those of nickel.

Preparation of some Aluminium Compounds and their Corresponding Hydrogen Derivatives.—M. Fonze-Diacon.—The author describes a rapid and novel method of preparing aluminium sulphide by the action of sulphur vapour on aluminium filings. He also obtains aluminium selenide in the pure state, and was able to prepare a phosphide and arsenide of aluminium—bodies which had not previously been obtained. Antimony will also combine with aluminium, but with great difficulty. Finally, the author describes the means of obtaining, owing to the easy decomposition of the above compounds by water, large quantities of SH_2 , SeH_2 , PH_3 and NH_3 ; also in the same way, but in less quantity, antimony hydride.

Estimation of Thallium.—V. Thomas.—The method for the estimation of thallium suggested by the author is based on the transformation of the salts of the protoxide into the salts of the peroxide, but it has the advantage of extreme simplicity and of a greater accuracy than the old methods. Bromide of gold is the oxidising agent used—or, more exactly, bromo-auric acid. By reduction, the gold bromide loses 3 atoms of bromine and gives a metallic deposit of gold, which can be weighed. When the reduction is ended, it is found that 2 atoms of gold correspond to 3 atoms of thallium.

Action of Anhydrous Aluminium Chloride on Acetylene.—E. Baud.—Pure dry acetylene is completely absorbed by aluminium chloride, even in the cold, when in a closed vessel. If heated to 70°, absorption is total in some minutes. A different reaction occurs when a current of acetylene is passed over the hot chloride. The chloride at first becomes heated, then, when the temperature reaches 70°, vapours are produced, and a reddish sublimate forms, which finally becomes black. The gaseous current is almost all absorbed, and there is a considerable

development of heat. The temperature is then raised to 120–130°, and the current of gas continued until there is no increase in weight of the sublimate. The two products formed have been analysed, and apparently have the composition $(C_{20}H_{15})_7 \cdot Al_2Cl_6$ and $(C_{20}H_{15.6})_7 \cdot Al_2Cl_6$.

Some New Organo-metallic Compounds of Magnesium, and their Application to the Synthesis of Alcohols and Hydrocarbides.—V. Grignard.—Methyl iodide attacks magnesium very slowly in the cold, but when a little anhydrous ether is added to the iodide a lively reaction takes place, a clear slightly coloured liquid results, with practically no deposit; this is a solution of the magnesium compound in ether, and contains one atom of magnesium dissolved in one molecule of methyl iodide. The author prepares also a certain number of secondary and tertiary alcohols. With the fatty halogen ethers the results are excellent.

Santalenes and Santolols.—M. Guerbet.—In a previous paper the author showed that the essence of oriental Indian santal contains, amongst other products, two isomeric carbides of formula $C_{15}H_{24}$, the α and β santalenes, and that the alcoholic portion probably consists of the two corresponding alcohols, the α and β santolols $C_{15}H_{26}O$. The present paper contains an account of experiments which led to the confirmation of the latter fact and the properties of the different products in a more perfect state of purity.

Tyrosinase.—C. Gessard.—Tyrosinase oxidises tyrosine with production of the red colour, which is also the effect of oxidation by a chemical agent (Millon's reaction). The blackening, as also the formation of the black precipitate, is a secondary phenomenon, depending on the elements which accompany diastase under natural conditions, and which pass with it into the solutions; this black colour can now be obtained at will.

MISCELLANEOUS.

Nitration of Benzoic Acid and of its Ethers.—A. E. Holleman.—The author has improved on the method previously given for the estimation of the component parts of a mixture of the ortho-, meta-, and para-nitrobenzoic acids, and has applied it to the study of the nitration of benzoic acid. The results are given briefly in the following table:—

		Nitration at—		
		–38°.	+8°.	+38°.
Ortho acid		14.4	18.5	22.3
Meta "		85.0	80.2	76.5
Para "		0.6	1.3	1.2

Strange bodies are not formed. The author has also studied the nitration of the benzoates of methyl and ethyl; he has observed that in this case also we obtain a mixture of the three isomers.—*Rev. Trav. Chim. P.-B.*, xviii., p. 267.

Preparation of Formose by means of Hydrated Oxide of Lead.—C. A. L. de Bruyn and A. van Ekenstein.—Heat for an hour on the water-bath a mixture of 500 c.c. of formol (at 40 per cent), 5 litres of water, and 20 grms. of hydrated oxide of lead; evaporate, and take up with a mixture of ethylic and methylic alcohols, and precipitate the salts of lead formed by the addition of ether; filter, and distil. The hydrated oxide of lead is prepared by precipitating the basic acetate with potash, and drying at the ordinary temperature after thorough washing. If we precipitate with NH_3 , the oxide obtained possesses no condensing action. Neither potash, soda, or the hydrates of the oxides of zinc, copper, and cadmium react on formol; with lime (30 per cent of the weight of the

aldehyde), only 20 per cent of the aldehyde is transformed into formose, while with hydrated amorphous oxide of lead the return reaches 70 per cent.—*Rev. Trav. Chim. P.-B.*, xviii., p. 309.

Opoponax.—A. Knit.—The composition of this resin is as follows:—The first part, soluble in ether, comprises an ether of ferulic acid and of oporesinotannol; the second part, insoluble in ether, comprises the free oporesinotannol, a gum, an essence, free ferulic acid, vanilline, and bassorine. The oporesinotannol alcohol gives a monobenzoylised derivative answering to the formula $C_{12}H_{13}O_2(OH)$. The gum, which does not act on polarised light, corresponds to the formula $C_8H_{14}O_7$. The essential oil gives a crystalline body, $C_{20}H_{10}O_7$, fusible at 133–134°, soluble in warm water, and having an acid reaction. Opoponax is characterised by this double fact:—(1). That it contains a resinotannol, the molecule of which contains 6 atoms of C of the same centesimal composition as that of Siamese benzoin; and (2) that it belongs to the group of resins which do not give ombelliferone by distillation. As a complement to this research the author has also analysed galbanum, but without having been able to isolate the galbanic acid described by Hirschsohn. As galipot readily gives this acid, the author is of the opinion that galbanum may contain this resin in the form of an impurity. Galbanum, the same as sumbul root, gave ombelliferone on analysis.—*Arch. d. Pharm.*, cccxxvii., p. 256.

The Action of Nitric Acid on the Saturated Carbides.—V. Markovnikof.—In previous papers the author has shown that concentrated HNO_3 acts very slowly at the ordinary temperature on the normal paraffins, but that it reacts easily on the saturated hydrocarbides containing a tertiary H. His research on trimethylethylmethane has shown that concentrated HNO_3 also only reacts very slowly in the cold on the carbides of the type R_3C , where R represents CH_3 or a normal radical $CH_3(CH_2)_n$; to all appearance the reaction becomes a little easier as the chain $CH_3(CH_2)_n$ lengthens, but it never becomes rapid. On penta-, hexa-, and heptamethylene, HNO_3 , or a mixture of HNO_3 and H_2SO_4 , only reacts at 100°; but with the substituted polymethylenes (containing tertiary H) nitric acid alone behaves as with the paraffins containing tertiary H; the sulphonic mixture, on the contrary, requires a slight elevation of temperature. Continuing, the author gives a practical method for detecting the presence of carbides containing tertiary H in a mixture of saturated carbides, and for effecting quantitative estimations.—*Journ. Soc. Phys. Chem. R.*, vol. xxxi., p. 530.

The Action of Acetylene on Copper.—H. Alexander.—Acetylene has no action in the cold on pure precipitated copper; but when the temperature is kept at about 240° to 250°, the gas is absorbed with the formation of small quantities of a greenish liquid, having the smell of a hydrocarbide, and a solid body of a bright brown colour, similar to cork in appearance, which gradually fills and finally obtrudes from the back end of the tube. No trace of acetylene has been obtained from this substance which is not soluble in any reagent. When heated in air, it gives off yellowish fumes, smelling of Stockholm tar, and then takes fire and burns with brilliant incandescence. It contains about 2 per cent of copper, which, however, can be eliminated by means of hydrochloric acid and ferric chloride, without any alteration in the properties of the substance. Further experiments are necessary to determine the constitution of this body. Provisionally the author recognises that the copper plays the rôle of contact agent, and effects the molecular condensation of the acetylene in the form of this hydrocarbide resembling cork. The hydrogen resulting from this condensation does not escape in the free state, but helps in the formation of the liquid smelling of petroleum, which has been mentioned above.—*Berichte*, xxxii., p. 2381.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Indiarubber.—Can you inform me of a good book treating the subject of quantitative analysis of manufactured indiarubber?—W. A. W.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Microscopical, 8. Demonstration on the Structure of some Palaeozoic Plants, with Sections of the Plants thrown on the Screen, by William Carruthers, F.R.S., President.

Institution of Mining and Metallurgy, 8. "On the Extraction of Gold from Auriferous Pyrites by Amalgamation," by T. G. Davey. "Notes on Gold-bearing Gravels," by W. S. Welton. "On the Treatment of Kalkgoorlie Sulphotelluride Ores," by Alfred James.

THURSDAY, 21st.—Chemical, 8. Ballot for the Election of Fellows. "Notes on the Chemistry of Chlorophyll," by L. Marchlewski, Ph.D., and C. A. Schunck. "Researches on Morphine—I," by S. B. Schryver, D.Sc., and F. H. Lees. "A New Series of Pentamethylene Derivatives—I," by W. H. Perkin, jun., F.R.S., J. F. Thorpe, Ph.D., and C. W. Walker. "Experiments on the Synthesis of Camphoric Acid—III. The Action of Sodium and Methyl Iodide on Ethyl-dimethylbutane Tricarboxylate," by W. H. Perkin, jun., F.R.S., and J. F. Thorpe, Ph.D. "On the Oxime of Mesoxamide and some Allied Compounds," by Miss M. A. Whiteley, B.Sc. "The Oxypheoxy- and Phenyleneoxy-acetic Acids," by W. Carter and W. T. Lawrence, B.A., &c. "The Condensation of Ethyl- α -bromo-isobutyrate with Ethyl Malonates and Ethyl Cyanacetates:— α -Methyl- α' -isobutylglutaric Acid" and "Methylisomethylsuccinic Acid—II," by W. T. Lawrence, B.A., &c.

FRIDAY, 22nd.—Physical, 8. (In the Rooms of the Chemical Society). "Notes on Gas Thermometry," by Dr. P. Chapuis. "A Comparison of Impure Platinum Thermometers," by H. M. Tory. "On the Law of Cailletet and Mathias and the Critical Density," by Prof. J. Young, F.R.S.

TO CORRESPONDENTS.

A. W. Comber.—Apply to the Assistant Secretary of the Chemical Society, Burlington House.

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MICHAELMAS TERM.—Monday, October 1, to Saturday, December 15.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2117.

SOME NEW OBSERVATIONS ON THE STATIC DIFFUSION OF GASES AND LIQUIDS, AND THEIR SIGNIFICANCE IN CERTAIN NATURAL PROCESSES OCCURRING IN PLANTS.*

By HORACE T. BROWN, F.R.S., LL.D., and F. ESCOMBE, B.Sc., F.L.S.

THIS paper is intended to be the first of a series descriptive of the work carried out by the authors in the Jodrell Laboratory on the fixation of carbon by green plants, and deals mainly with the purely physical processes by which atmospheric carbon dioxide gains access to the active centres of assimilation.

The new evidence which F. F. Blackman brought forward in 1895 in favour of the gaseous exchanges of leaves taking place exclusively through the stomatic openings, presents at first sight certain difficulties of a physical nature, which have led to an examination of the whole question of the free diffusion of carbon dioxide at very low tension, and under a set of conditions very different from those under which the previous determinations of the coefficient of diffusion of carbon dioxide and air have been made by Loschmidt and others, where the gases were initially of equal tension, and the ratios of mixture departed widely from those of ordinary atmospheric air. The inquiry has led to the discovery of some new facts connected with the static diffusion of gases and liquids, which are of considerable interest, not only from the physical point of view, but from the explanations they suggest of certain natural processes which are primarily dependent on diffusivity.

The method employed in the first instance for the determination of the diffusivity of atmospheric carbon dioxide was one of *static diffusion* down a column of air of a definite length, towards an absorptive surface at the bottom of the column. When a static condition has been established, there is a steady flux of the carbon dioxide down the air column which may be quantitatively investigated by the same simple mathematical treatment as the "flow" of heat in a bar when the permanent state has been reached, or the "flow" of electricity between any two regions of a conductor maintained at a constant difference of potential.

By a long series of experiments of this nature it was found that the diffusivity constant, k , for very dilute CO_2 does not materially depart from the value assigned to it by Loschmidt and others, when experimenting with much higher ratios of mixture, and that the difference is certainly not of sufficient magnitude to be taken into serious account in the study of the natural processes of gaseous exchange in the assimilating organs of plants.

In the static diffusion of a gas, vapour, or solute, as the case may be, the amount of substance diffusing in a given time, all other conditions being the same, is directly proportional to the sectional area of the column. It is found, however, that if the flow is partially obstructed by interposing at any point in the line of flow a thin septum pierced with a circular aperture, the rate of flow across unit area of the aperture is greater than it would be across an equal area of the unobstructed cross-section of the column at this point. If the margin around the aperture has a width of at least three or four times its diameter, the rate of flow is now found to be directly proportional to the *linear dimensions* of the aperture and not to its area,

so that the velocity of flow through unit area varies inversely as the diameter.

A large number of experiments on the diffusion of carbon dioxide, water-vapour, and sodium chloride in solution, are given in support of this proposition. All these show that the rate of diffusion across such a septum, all other conditions being the same, is directly proportional to the diameter of the aperture, and not, as might have been expected, to its area.

Exactly the same result is obtained when small circular discs of an absorbent, such as a solution of caustic alkali, are surrounded by a wide rim and exposed to *perfectly still* air, the amount of carbon dioxide absorbed under these conditions being proportional to the *diameters* of the discs.

If, however, there are any sensible air currents the absorption becomes proportional to the areas.

These two sets of phenomena may be explained as follows:—

In the case of the absorbing disc in perfectly still air, the convergent streams of carbon dioxide creep through the air towards the absorbing disc, establishing a steady gradient of density, and this creep will be a flux perpendicular to the lines of equal density, which form curved surfaces or "shells" surrounding the disc and terminating in the rim. The state of things is exactly analogous to the electric field in the neighbourhood of a conductor of the same shape and dimensions as the absorbent disc.* In the case of the gas, the curves or "shells" of equal density are the analogues of the similarly curved surfaces of equipotential above the electrified disc, whilst the converging lines of creep or flux of the gas are the analogues of the lines or tubes of force which bend round into the disc as they approach it.

If we consider two such absorbent discs of different diameters, the curved surfaces in each system corresponding to a given density will be found at actual distances from the discs, which are in the same proportion to each other as are the diameters of the discs. In other words, the gradient of density on which the rate of flow depends will be proportional to the diameters of the discs, which is exactly what is found experimentally.

This case of an absorbent disc is the exact converse of one which has been theoretically investigated by Stefan, viz., the conditions of evaporation of a liquid from a circular surface. He found that the lines of flux of the vapour proceeding from the surface of the liquid must be hyperbolas, whilst the curved surfaces of equal pressure of the vapour must form an orthogonal system of ellipsoids, having their foci, like the hyperbolas, in the bounding edges of the disc. This was a purely mathematical deduction which has never been verified experimentally, but it will be seen that the exactly converse phenomena of diffusion are in complete agreement with it.

In the other case of a diffusive flow through a circular aperture in a diaphragm, the lines of flow, which are *convergent* as they approach the aperture, bend round their foci situated in the edges of the disc and form a *divergent* system on the other side. If the chamber into which they pass is a perfectly absorbent one, and is sufficiently large, there will be formed on the inner side of the diaphragm a system of density shells similar to those outside, but with the gradient of density centrifugally instead of centripetally arranged. This system of shells is termed negative, and is as effective as the outer positive system in regulating the flow according to the "diameter law," so that this law will still hold good, even if the outer air currents are sufficient to sweep away the external positive shells altogether.

All the known facts of diffusion through circular apertures in a diaphragm are in complete accord with the above explanation, which is fully elaborated in the original paper.

* Abstract of a Paper read before the Royal Society, June 14, 1900

* The authors are indebted to Dr. Larmor for this suggestion of the electrostatic analogy.

By diffusing colouring matter through apertures in a septum, under such conditions as to prevent convection currents, the "density shells" have been rendered visible, and it has been shown that their ellipsoidal form is exactly that which is demanded by the above hypothesis. Moreover, this method gives an experimental demonstration of the more rapid projection of the diffusing particles from the edges of the aperture than from a point nearer its centre, a fact completely in harmony with the deduction of Stefan regarding the evaporation of liquids under analogous conditions.

The various cases which present themselves in practice with regard to the rate of diffusion through single apertures in a diaphragm are then discussed from the above point of view, and simple formulæ for the determination of this rate for single and double systems of density shells are established: (1) for cases where the thickness of the diaphragm is negligible, and (2) for other cases where the apertures become more or less tubular. In a subsequent section of the paper it is shown how closely the observed facts conform to these deductions, and that in static diffusion through apertures in a septum we have a new and accurate method for the determination of the diffusivity constants of atmospheric CO_2 , of the vapours of liquids, and of substances in a state of solution.

Since the velocity of the diffusive flow through unit area of an aperture in a diaphragm varies inversely with the diameter, it might reasonably be expected that a diaphragm could be so perforated with a series of very small holes arranged at suitable distances from each other, as to exercise little or no sensible obstruction when it was interposed in a line of diffusive flow, although the aggregate area of the small holes might represent only a small fraction of the total area of the septum. Multiperforate diaphragms of this kind were found to possess all the remarkable properties which had been anticipated.

The material used for the septa was very thin celluloid, which was perforated at regular intervals with holes of about 0.38 m.m. in diameter. Details of a number of experiments with such diaphragms are given, in which it is shown that they may be so arranged as to produce but little obstructive influence on the diffusive flow of a gas when the total area of the apertures amounts only to about 10 per cent of the area of the septum, and that nearly 40 per cent of the full diffusive flow may be maintained when the number of the apertures is so far reduced as to represent an area of only 1.25 per cent of the full area of the septum.

The explanation is to be found in the local intensification of the gradient of density in the immediate neighbourhood of the diaphragm, and which does not extend to the column away from the apertures. This disturbance of gradient is brought about by the rapid convergence of the lines of flux, and their divergence on the other side, with the consequent formation of a system of "density shells" over each aperture. A system of perforations of this kind may be compared with a system of conductors electrified to a common potential, the density of the diffusing substance above the apertures corresponding to electric potential, and the non-absorbing portions of the diaphragm to a surface formed by lines of electric force. Just as the electric capacity of a plate is not much reduced by cutting most of it away, so also is it possible to block out a large portion of the cross section of the diffusing column without materially altering the general static conditions on which the flow depends.

The importance of these results in relation to diffusion through porous septa is next considered, diffusion through a thin porous septum being only an extreme case of free diffusion through a multiperforate diaphragm, whose apertures are so far reduced in size as to materially interfere with the mass movement of the diffusing substance.

A section of the paper is devoted to the application of these new observations to the processes of gaseous and liquid diffusion in living plants, and it is pointed out that the structure of a typical herbaceous leaf illustrates in a

striking manner all the physical properties of a multiperforate septum. Regarded from this point of view it is shown that the stomatal openings and their adjuncts constitute even a more perfect piece of mechanism than is required for the supply of carbon dioxide for the physiological needs of the plant, and instead of expressing surprise at the comparatively large amount of the gas which an assimilating leaf can take in from the air, we must in future rather wonder that the intake is not greater than it actually is.

From data afforded by actual measurements of the various parts of the stomatal apparatus of the sunflower, it is shown that an extremely small difference of tension of the carbon dioxide within the leaf, as compared with that in the outer air, will produce a gradient sufficient to account for the observed intake during the most active assimilation.

It is also shown that the large amounts of water-vapour which pass out of the leaf by transpiration are well within the limits of diffusion, and that it is unnecessary to assume anything like mass movement in the outgoing vapour.

The translocation of solid material from cell to cell in the living plant is next considered, especially with reference to this transference, being, at any rate in part, brought about by means of the minute openings in the cell-walls through which the connecting threads of protoplasm pass. Notwithstanding the very small relative sectional area of these perforations they probably exercise an important function in cell-to-cell diffusion, in virtue of their properties as multiperforate septa.

There are two appendices to the paper, one in which a full description is given of a series of experiments on the absorption of carbon dioxide by solutions of caustic alkali from air in movement; the second being devoted to a detailed description of the methods used for accurately determining the carbon dioxide absorbed.

PREPARATION OF AN AMMONIACAL SOLUTION OF CUPROUS CHLORIDE, BY MEANS OF HYDROXYLAMINE, FOR THE DETECTION OF ACETYLENE.

By L. ILOSVAY VON N. ILOSVAY.

HYDROXYLAMINE is a very convenient substance to use for the reduction of cupric chloride to cuprous chloride; but the colour of the precipitate produced by acetylene in a similar solution varies considerably with the proportions of the constituents.

The author proposes to prepare the solutions necessary for the detection of acetylene by means of the three following formulæ:—

1. Cupric chloride ($\text{CuCl}_2 \cdot 3\text{H}_2\text{O}$) .. 0.75 grm.
Chloride of ammonium 1.5 grms.
Chlorhydrate of hydroxylamine .. 2.5 "
Ammonia (20 per cent NH_3) .. 3 c.c.
2. Cupric nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$] .. 1 grm.
Hydrochlorate of hydroxylamine .. 3 grms.
Ammonia (as above) 4 c.c.

3. Like No. 2, but the cupric nitrate is replaced by crystallized sulphate of copper.

The copper salt is dissolved in a little water in a 50 c.c. flask; the ammonia is added drop by drop, then the salt of hydroxylamine; shake carefully and make up the volume to 50 c.c. In a few minutes the solution becomes colourless and is then ready for use. It will keep well for two or three days, but at the end of this time its sensibility gradually diminishes.

Acetylene is tested for in illuminating gas by shaking up a few cubic centimetres of this solution with half a litre

of gas, or by passing the gas through a tube containing wadding or glass-wool impregnated with the reagent. The nitrate solution is the most sensitive, but the precipitate formed seems to be less stable than that obtained with the other solutions.—*Berichte*, xxxii., p. 2697.

A NEW METHOD FOR THE ESTIMATION OF MORPHINE IN OPIUM.

By H. M. GORDIN and A. B. PRESCOTT.

ALL the alkaloids of opium may be set free by ammonia. After a sufficient maceration the liquid is evaporated, and the narcotine, codein, thebain, papaverine, and most of the other bases soluble in C_6H_6 are removed by means of this solvent. The morphine, which is insoluble in C_6H_6 , is removed by a mixture of $CHCl_3$ and C_2H_6O . The solvent is evaporated, the residue dissolved in a solution of 1/20th normal acid, and the excess of acid titrated by a solution of 1/20th normal KOH. This method can be checked by a titration with iodine on the product of the above estimation. It suffices to treat it with $Ca(OH)_2$, acidulate, and add a solution of titrated iodine; one molecule of morphine fixes 3 atoms of iodine, giving the compound $C_{17}H_{19}NO_3HI_3$. The iodine in excess can be estimated with $S_2O_3Na_2$. Both methods give identical results.—*Archiv d. Pharm.*, ccxxxvii., p. 380.

ON SELENIFEROUS SULPHURIC ACID.

By MM. SCHLAGDENHAUFFEN and PAGEL.

WHILE preparing pure hydrochloric acid for laboratory use, by means of decrepitated or fused chloride of sodium and sulphuric acid, labelled pure as in the usual manner, we were astonished to find that the water in the wash-bottle became coloured red. The tint became deeper and deeper as the operation continued, and at the end of a certain time quite a noticeable deposit was produced. This latter soon disappeared, and the liquid again became colourless. If we then passed a current of sulphurous acid through the solution, a brick-red precipitate was again formed, analogous to the one first observed.

This deposit is due to nothing else but selenium. It can only come from the chloride of sodium or the sulphuric acid. Now, as the solution of the salt used did not undergo any change under the influence of a current of sulphurous acid, it is beyond doubt that the presence of the selenium could only be due to an impurity in the sulphuric acid.

Different samples of sulphuric acid, obtained from the makers at Nancy, having given us the same results, we looked about for other samples with the object of repeating the experiments. We were surprised to find that out of ten samples, labelled both pure and ordinary, there were only three which did not give first the red colour, and then a more or less abundant deposit after being heated for some time.

All the commercial acids examined during this period thus contained selenium, and the commercial processes now in use for getting rid of the arsenic are shown to be insufficient for removing the selenium at the same time.

One sample only, prepared by ourselves in our own laboratory, and rectified over bichromate of potassium, did not give this reaction, and was thus free from the impurity.

To detect this metalloid in sulphuric acid, it is not necessary to operate on a large quantity of acid at a time; a few drops are sufficient; in fact, as selenious acid, treated with concentrated sulphuric acid, has the property of colouring codein, first an intense green, then blue, we thought that this very characteristic reaction might be utilised in this particular case, the more so as

pure sulphuric acid alone does not give the colouration with codein.

Thus, if we pour 5 or 6 drops of sulphuric acid over a fragment of codein, and if, after the lapse of a few minutes, there appears a green colouration in the cold, changing to a greenish blue on the water-bath, we may be certain that selenium is present in the acid under examination.

This sensitive reaction is of the same kind as that long known for detecting the presence of nitrated products in sulphuric acid, by means of the rose-colour obtained by placing the acid in contact with a fragment of brucine.—*Journ. Pharm. et Chim.*, Series 6, vol. xi., No. 6.

THE PURIFICATION OF ACETYLENE BY MEANS OF ACID SOLUTIONS OF CHROMIC ACID.

DOUBTS having been thrown on the efficacy of Ullmann's method of purifying acetylene by means of an acid solution of chromic acid, the inventor has published the results of some experiments carried out by Dr. Wachs, of Carlsruhe, which prove the efficacy.

Two glass tubes, 40 c.m. in height, were filled with pumice-stone impregnated with a solution obtained by dissolving 1 part of crystallised chromic acid in 2 parts of acetic acid at 50 per cent. Through these tubes was passed a quantity of acetylene containing 0.5066 grm. of phosphorus per cubic metre; the gas was then passed through a tube of smaller dimensions filled with lime and sawdust to absorb all traces of acetic acid carried over by vapourisation. The gas thus purified did not contain a trace of phosphorus when the rate of flow was 29 litres per hour.

At a speed of 119 litres per hour, which is much higher than that advised by the inventor, the gas on leaving contained a small quantity of phosphorus.

The lighting power of the gas was determined before and after purification; it was practically the same.

It is stated that 5.5 grms. of chromic acid suffice to purify 1 cubic metre of acetylene, and that the cost of purification by this method represents 0.3 per cent of the cost of the carbide used for the production of the gas.

It has also been stated that Ullmann's method resembles that of Frank for the purification of acetylene. Ullmann, on the contrary, says that the acidulated solutions of the metallic salts, as used by Frank, retain the impurities, owing to the formation of insoluble or non-volatile compounds with the metals. Chromic acid acts quite differently; it oxidises the impurities instead of forming precipitates with them.

It has further been stated that in Ullmann's process the active body is not chromic acid, but a solution of chromic chromate. According to Ullmann, however, such a solution cannot exist, for, even if it were formed, it would immediately decompose into active chromic acid and an inactive chromic salt. Further, experiments have shown that an acidulated solution of chrome-alum will not completely remove the impurities from acetylene.

It may be pointed out that the estimation of the expense of the purification of acetylene by the various methods is not correct, as they do not give the analysis of the raw gas or its rate of flow, and, further, the purity of the gas obtained has not been proved by trustworthy experiments.

As reagents for determining the degree of purity of acetylene, Ullmann recommends:—1. An aqueous or slightly acid solution of acetate of lead at 10 per cent; 2. A solution of 1 part of bichloride of mercury in 10 parts of hydrochloric acid at 10 per cent.

The gas is passed through two wash-bottles containing respectively these two solutions. If it has been imperfectly purified, white rings form on the tube through which the gas comes, and finally the solutions become cloudy.—*Journ. f. Gasbeleuchtung*, xlii., [12], p. 198.

INFLUENCE OF FINELY-DIVIDED PLATINUM
ON THE COMBINATION OF HYDROGEN
AND OXYGEN.

By WM. FRENCH, M.A., F.I.C.

It has been long known that many mixtures of gaseous bodies can be readily made to combine chemically if they be in contact with spongy platinum (*e.g.*, a mixture of hydrogen and oxygen at ordinary temperatures, or hydrogen and bromine vapour, &c.); but, so far as I am aware, no work has been published previous to my preliminary experiments (*Proc. Chem. Soc.*, 1897, No. 175, p. 52) on the action of this so-called catalytic agent in presence of highly purified gaseous bodies, *i.e.*, gases in which all traces of moisture or other electrolyte have been removed.

The following work was therefore undertaken with a view of ascertaining, if possible, the part played by platinum in these changes. Most of the experiments were completed in 1897; since then, however, I have confirmed them, the whole of which are summed up below.

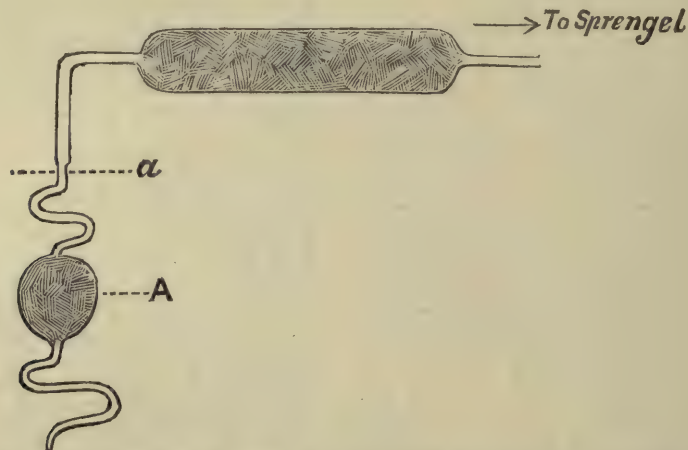
My first experiments consisted of allowing purified bromine vapour and hydrogen gas to come into contact with spongy platinum. The difficulties experienced were so many that I abandoned them *pro tem.* after the preliminary trials. The results obtained, however, were sufficiently

Charging the Drying Tubes.—Some of the potash drying tubes were connected, after charging, with a phosphoric oxide tube, which was connected to an exhaust pump. The combination was exhausted, and then air allowed to quickly enter, so that in passing over the phosphoric oxide it carried small particles forward, which became scattered on the fused potash; this I found made a very efficient drying tube. Some of the phosphoric oxide drying tubes were filled in the following way:—Some glass-wool was chopped as finely as possible with a knife, then placed in a wide-mouthed stoppered bottle, and heated in an air-bath to about 300° C., and cooled in a desiccator. After cooling until the bottle was just warm, about an equal volume of phosphoric oxide was added and the two thoroughly shaken together. By this method the quantity of oxide required was very greatly diminished, whilst the absorbing surface was largely increased. On some occasions, on using a tube containing this mixture, I noticed a smell of phosphine, and so abandoned this form of drying tube in my later experiments.

Description of Apparatus.

1. About 3 to 4 grms. of spongy platinum for each experiment were placed in a bulb of about 5 c.c. capacity and drawn out and bent as in A, Fig. 1. This was connected to a phosphoric oxide tube and Sprengel pump.

FIG. 1



satisfactory to induce me to continue the work, using the gases hydrogen and oxygen.

Briefly, these experiments consisted in allowing carefully dried hydrogen and oxygen gases (prepared electrolytically by a Bunsen decomposer) to come into contact with carefully purified and dried spongy platinum, both in presence and in absence of light.

DETAILS OF THE WORK.

Preparation of Spongy Platinum.—This was obtained from foil by solution in aqua regia, precipitation as double chloride with ammonium chloride, and careful ignition at as low a temperature as possible. This was well washed and dried *in vacuo* in contact with a tube of fused caustic potash.

Drying Reagents Used:—

1. *Re-distilled sulphuric acid.*
2. *Potash.*—Prepared by alcohol from Messrs. Hopkin and Williams, and fused as suggested by Dittmar and Henderson (*CHEMICAL NEWS*, lxxiii.).
3. *Phosphoric Anhydride.*—In some of my first experiments this was purified as suggested by Shenstone (*Journ. Chem. Soc.*, lxxiii.), but later on I used the purest, obtained from Messrs. Hopkin and Williams.

The bulb was placed in an air oven and heated for eight to twelve hours at a temperature of about 200° C. *in vacuo*, then sealed off at *a*, Fig. 1. The object of the bent drawn out ends was to insure rupture of the bulb, and consequent exposure of the platinum with the gases when necessary.

2. The sealed bulb containing the platinum, A, was next placed in a tube, B (Fig. 2), between two constrictions, *b b'*. This tube was about 50 c.m. long between the constrictions and 2 c.m. diameter. At each end of B, beyond the constrictions, was a well ground stopcock; beyond the stopcocks were drying tubes (C, D, E); C and D contained phosphoric oxide, whilst E contained caustic potash, and each tube was about 25 c.m. by 2 c.m.; F and G contained re-distilled sulphuric acid; G fitted into the decomposer, H, by a ground joint, I, and mercury trap, J. The end of the drying tube, C, was drawn out and bent, *c'*, so that it could be used as a delivery tube or connected to an exhaust pump. The whole apparatus had fused glass joints, and was about 200 c.m. long.

Experimental.

1. The tube *c'* was connected to a Sprengel's pump, and the ground-glass joint I, after removing from the mercury trap J, was attached to two or three wash-bottles, a current of air was then slowly drawn through the whole

apparatus for five to eight hours, whilst the whole of the tube B was heated to near the softening-point of glass; this was to ensure the removal of any gases, &c., adhering to the sides of the tube.

2. The joint I was now replaced in the mercury trap J, and a current from a three-celled battery passed through the decomposer for about two hours; the delivery tube *c'* was then placed beneath mercury in a trough, K, and the electrolytic gases passed for about eight to twelve hours.

Notes.—Tubes of the escaping gases were collected from time to time, and small quantities of spongy platinum added (this had not been previously dried as described above). In all cases the gases combined (if sufficient platinum were added) with an explosion, and in no case did I use more platinum than was actually used in the experiments, viz., 3 to 4 grms. But I noticed in all cases a certain interval of time to elapse between the addition of the platinum and the actual explosion. This interval seemed to me to be less in broad daylight, or when burning a piece of magnesium near to the tube, than at night when most of the experiments were carried out.

3. The whole apparatus, now filled with the electrolytic gases, was wrapped in black paper and allowed to stand for periods varying from three to six days (later on, in one experiment, I found one day sufficient to dry the gases); the stopcocks *b b'* remained open, so that the gases were in direct contact with the drying reagents.

the stopcock next to the plug was quickly opened and closed, so that an inrush of damp air was admitted; but in no case did I notice any sign of combination, even after fifteen minutes. In some cases more moist air was introduced, and in one or two cases a drop of water (distilled) added, yet no explosion was observed.

8. The tube was again divested of its paper cover, and exposed to strong light, as before; and only on one occasion* did I get any trace of an explosion, or sign of combination. In every case I now opened the tube, and applied a lighted match, and at once obtained a flash, showing that, even if combination had taken place at all, it must have been extremely slow.

Many circumstances have prevented me continuing the work, although I have made preliminary trials, using the gases NO_2 and H in presence of platinum, also HCl and O in presence of copper sulphate and pumice. Should I get the opportunity I intend continuing the work.

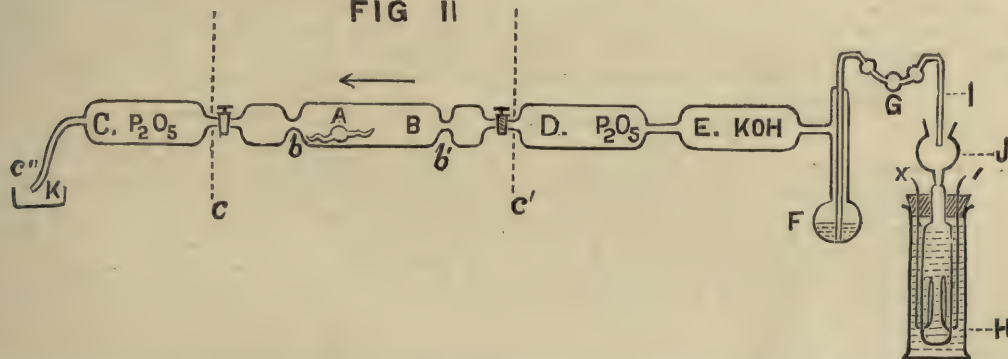
Conclusions.

1. Finely-divided platinum does not, by itself, bring about the combination of a mixture of purified hydrogen and oxygen at ordinary temperatures.

2. The combination of these gases, when not carefully dried, in presence of spongy platinum seems to be influenced by light.

It seems, then, that the so-called "catalytic action" of

FIG II



4. The stopcocks *b b'* were now closed, and the tube B separated from C and D by a file at *cc'*. B (being still wrapped in black paper) was shaken, so that the bulb A containing the platinum was smashed. In no case did an explosion occur, nor was there any appearance of a formation of dew, or heat evolution, even after a lapse of fifteen to twenty minutes.

5. The tube B was next divested of its wrapper and exposed to bright sunlight when available, or a strip of burning magnesium ribbon; still, in no case was there any appearance of chemical combination.

6. The tube B was then opened and a lighted match applied, and in all cases the mixture exploded.

These experiments, only differing slightly in detail, having been repeated so often, I was led to the conclusion that even if spongy platinum does bring about the combination of these gases by itself at ordinary temperatures, then the combination must be extremely slow, and, for an actual explosion to take place, a third body must also be present.

I next tried to find the conditions necessary for the gases to rapidly combine (i.e., explode); so far I have only tried the addition of one substance, viz., water, and even the results from this are not satisfactory.

The following gives a general result of the work in this direction:—

7. The tube B, still wrapped in paper, and containing the gases and platinum in contact, as obtained in 4, was cooled in a tube of water, and a plug of cotton-wool, damp with water, placed above one of the openings *cc'*;

spongy platinum, which is often regarded as a "surface action," may probably only be true when in presence of an electrolyte, as is possibly the case with many other mixtures of gaseous bodies, which, although they readily combine under ordinary circumstances, will not do so if quite pure and dried, as shown by Dixon, Baker, and others.

Since conducting the above experiments, which were all, with one exception, made previous to 1899, seeing that the action was evidently not by itself a truly surface action,—i.e., the energy necessary to bring about the change was not at any rate all derived from the condensation of the gases on the surface of the platinum.—I was led to roughly calculate the heat which would be generated, and the temperature to which the mixture of gases and platinum might be raised by such condensation. This I find is lower than 612°C ., which is given by Meyer as the point of ignition of the electrolytic gases.

Neumann says platinum sponge absorbs about fifty times (49.3) its own volume of hydrogen gas.

Now the greatest mass of platinum taken was never greater than 5 grms., and taking 20 as the sp. gr. of platinum, this would give 0.25 c.c. as the greatest volume of platinum taken for any individual experiment; therefore the volume of hydrogen condensed would not be greater than about 12 c.c. Then, taking sp. ht. of platinum as 0.032, and that for hydrogen as $\frac{1}{14}$, the increase

* In this particular case I fancied I had a trace of HCl on the cotton-wool plug.

in temperature of the mass (neglecting oxygen) is below 600° C., which is below the point of ignition of the mixture.

Grammar School, Bury.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY CONVERSAZIONE.

ON Wednesday evening (June 20th) the second Conversazione, known as "the Ladies' Night," was held at the Royal Society's Rooms at Burlington House, the Fellows and guests being received by the President, The Lord Lister, F.R.C.S., D.C.L.

Among the numerous and interesting exhibits we may mention that of Prof. RAMSAY and Dr. TRAVERS, who showed the following:—

(1). The Inert Atmospheric Gases; their Spectra, and some of the Apparatus Used in Determining their Physical Properties.

Spectrum of—	Density.	Atomic weight.
Helium	1'98	3'96
Neon	about 10	about 20'0
Argon	19'96	39'92
Krypton	40'77	80'54
Xenon	64'0	128'0

(2). Apparatus for Determining the Molecular Volume of these Elements in the Liquid State.

(3). Apparatus for Distilling the Gases Fractionally; Fractionation of Atmospheric Air.

(4). Bulbs in which the Densities of the Gases have been Determined.

Mr. J. MACKENZIE DAVIDSON, M.B., exhibited a Stereoscopic Fluoroscope, by means of which an observer is enabled to see the shadows cast by Röntgen rays on the fluorescent screen in stereoscopic relief. With this instrument, a bullet or needle, &c., can be seen in its true position and its anatomical relations observed, and the surgeon can easily touch the bullet, &c., with a probe or forceps, while he is looking at its shadow on the screen; the position of a Mauser bullet in a leg of mutton was distinctly found by this means.

The same gentleman also showed a Rotatory Mercury Break, with which good results are obtained with from 12 volts up to 100, according to the speed of rotation.

The Eclipse Committee of the British Astronomical Association showed a number of interesting Drawings and Photographs of the Total Eclipse of the Sun on the 28th of May last.

A further number of Photographs and Drawings of the same subject were also exhibited by the Royal Astronomical Society and the Joint Permanent Eclipse Committee of the Royal and Royal Astronomical Societies.

Prof. SILVANUS THOMPSON, D.Sc., showed some experiments on the Aberration called *Coma*. *Coma* is an aberration due to the several zones of the lens not having equal focal lengths, and hence, when the lens is transmitting an oblique pencil, the unequal refraction of the different parts gives rise to a singular unilateral distortion of the cones of rays traversing the various zones. The actual path of the rays was very distinctly shown by means of a smoke box which they traversed.

Mr. W. GOWLAND exhibited some Remains of a Roman Silver Refinery found at Silchester. The hearths, which are now saturated with lead and copper oxides, were constructed of bone-ash; they are of special interest, being the only examples of Roman cupellation furnaces of that material which have been found.

Professor HELE-SHAW and Mr. HAY exhibited at the May Soirée of last year some experiments in stream line

motion which were analogous to lines of magnetic induction. These were produced by the method of thin films of variable thickness, the greater depth corresponding to greater permeability of the analogous magnetic body. Since that period the accurate measurement and calculations necessary for determining to what degree these results corresponded to the known laws of magnetic induction have been carried on. A paper read before the Royal Society, on Thursday, the 21st inst., gives a full account of this work, and also of the improvements in the actual appliances used, which latter may be stated briefly to be—

1. The use of a translucent medium which can be accurately shaped and made of a required thickness with a perfectly true surface.
2. The adoption of a specially constructed glass plate by which a large number of results may be more readily obtained with comparatively little trouble, and which will enable the method to be generally adopted for educational work, as well as for purposes of research.

Prof. RAY LANKESTER showed some enlarged models of Gnats and of Human Blood Corpuscles Infected by the Malaria Parasite; these latter are magnified seven thousand five hundred times.

Three demonstrations, with experiments and lantern slides, were given in the Meeting-room, viz., Cinematograph Photographs of Native Dances in Torres Straits, by Prof. HADDON; the production of Short Electric Waves and the Study of Electro-optic Phenomena, by Prof. J. A. FLEMING; and the Life-history of the *Cicindela campestris*, —the Common Tiger Beetle.

CHEMICAL SOCIETY.

Ordinary Meeting, June 7th, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

MESSRS. T. G. Joyce, A. W. Bain, T. FitzGibbon, and B. Jordan-Smith were formally admitted Fellows of the Society.

The following certificate was read for the first time:—Edmund Foster Hudson, Churcher's College, Petersfield, Hants.

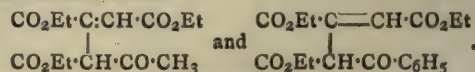
Professor DUNSTAN, on behalf of the Society, congratulated the President on the distinction recently conferred upon him by Her Majesty.

The PRESIDENT returned his thanks to the Society for their congratulations.

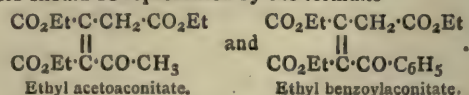
Of the following papers, those marked * were read:—

*75. "Condensation of Ethyl Acetylenedicarboxylate with Bases and 8-Ketonic Esters." By S. RUHEMANN and H. E. STAPLETON.

The esters previously obtained (*Trans.*, 1896, lix., 530, 1383; 1897, lxxi., 323) by the action of ethyl acetoacetate and ethyl benzoylacetate on ethyl chlorofumarate had been formulated thus:—



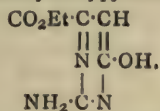
These esters were found by the authors to be identical with those which are formed by using ethyl acetylenedicarboxylate instead of ethyl chlorofumarate (*Trans.*, 1899, lxxv., 784). The considerations brought forward (*Trans.*, 1900, lxxvii., 242) led to the conclusion that these esters should be represented by the formulæ—



The latter expressions are in harmony with the facts

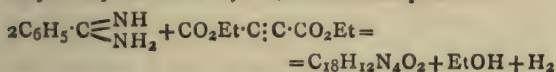
that these esters do not give a colouration with ferric chloride and that the same substances are produced by using chlorofumaric and chloromaleic esters (*Trans.*, 1896, lix., 530).

The difference in the behaviour of ethyl acetylenedicarboxylate from that of ethyl phenylpropiolate is also found in its reactions with guanidine and benzamidine. The former base yields with it a cyclic compound which has both basic and acidic properties, and is regarded by the authors as ethyl amidohydroxypyrimidinecarboxylate,—

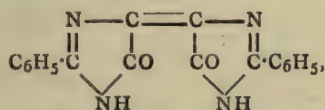


This ester, on boiling with potassium hydroxide, hardly undergoes any change beyond hydrolysis to the corresponding acid.

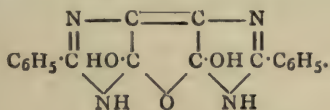
Quite unexpected is the reaction of benzamidine with ethyl acetylenedicarboxylate, which takes place thus—



(the hydrogen probably effects a reduction), producing ruby-red crystals of a substance called *glyoxaline red*. Its constitution is probably—



which indicates the close relationship of this compound to indigo and pyrazole blue. Glyoxaline red, when boiled with glacial acetic acid, takes up one molecule of water, and is transformed into a substance, $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_3$, crystallising in yellow needles, for which the authors suggest the formula—

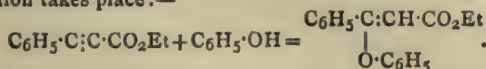


This compound dissolves in potassium hydroxide, forming a yellow solution, which gradually acquires the red-violet colour of the alkaline solution of glyoxaline red.

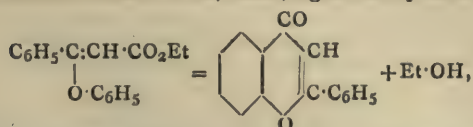
The authors have found that the same substances are formed from guanidine as well as from benzamidine by using ethyl chlorofumarate instead of ethyl acetylenedicarboxylate.

*76. "Condensation of Phenols with Ethyl Phenyl propiolate." By S. RUHEMANN and F. BEDDOW.

The ease with which the esters of the acetylene series form additive products induced the authors to study their behaviour towards phenols. They find that the sodium phenoxides readily combine with ethyl phenylpropiolate to form aryl derivatives of ethyl β -hydroxycinnamate; thus in the case of sodium phenoxide itself the following reaction takes place:—

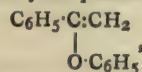


It was hoped that these esters might be converted into flavone and its derivatives, according to the equation—

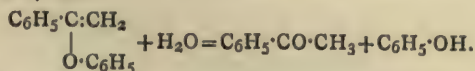


but up to the present this has not been accomplished, because the esters are so easily hydrolysed to the corre-

sponding acids, whilst the acids themselves, on heating, lose carbon dioxide and yield phenoxystyrene,—



and its homologues; further, on warming phenoxystyrene with dilute acids, it decomposes into acetophenone and phenol, thus—



The homologues of phenoxystyrene decompose in a similar manner.

The authors found that ethyl phenylpropiolate reacts with the sodium derivatives of *o*- and *p*-cresol to form compounds analogous to those obtained with sodium phenoxide. The α - and β -naphthols also react in a similar manner with the ester, and form the ethyl esters of the naphthoxycinnamic acids; thus from α -naphthol ethyl α -naphthoxycinnamate and the corresponding acid were prepared; this acid seems to be less stable than those obtained from phenol and the cresols, as it undergoes decomposition when left in contact with dilute sulphuric acid, acetophenone being produced.

*77. "The Constitution of Pilocarpine." By H. A. D. JOWETT, D.Sc.

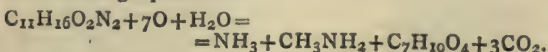
In a recent paper (*Trans.*, 1900, lxxvii., 494), the author gave an account of some preliminary experiments on isopilocarpine, and reserved the question of the constitution of the alkaloid for a future paper. Owing to the publication of a paper on pilocarpine by Pinner and Kohlhammer (*Ber.*, 1900, xxxiii., 1424), the author has deemed it advisable to give a brief account of the results he has thus far obtained.

Action of Fused Potash on Isopilocarpine.—It was shown (*loc. cit.*) that ammonia, methylamine, and an acid, probably isobutyric, were formed in this reaction. It has now been proved that isobutyric acid is formed, in addition to other acids which are produced in quantity too small to be identified.

Distillation of Pilocarpine with Soda-lime.—A preliminary experiment had shown that the bases formed in this reaction are ammonia and either 2- or 3-methylpyridine. Further investigation has shown that, in addition, methylamine is formed, and that only a very small quantity of 3-methylpyridine is produced. As the formation of traces of a pyridine base by distillation with soda-lime does not throw very much light on the constitution of the alkaloid, this reaction has not been further investigated.

Oxidation of Isopilocarpine by Potassium Permanganate.

—The oils previously mentioned have now been examined, and it has been proved that the products of oxidation, besides ammonia and methylamine, are acetic acid and an acid having the formula $\text{C}_7\text{H}_{10}\text{O}_4$. The quantity of permanganate required for the oxidation is about 6 molecular proportions, and the reaction may be expressed by the following equation:—



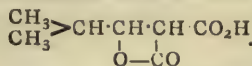
The new acid was obtained as the ethyl ester, and the yield was 70 per cent of the theoretical. The acid is a very slightly coloured yellow oil, with a peculiar smell, and boils at 210° – 220° at 10 m.m. pressure. By titration, it was shown to be a laëonic acid.

The ethyl ester, $\text{C}_{13}\text{H}_{20}\text{O}_4$, boils at 299° at atmospheric pressure, is optically active, $[\alpha]_D^{15} = +30.76^\circ$, and has a specific gravity 1.1053 ($15^\circ/15^\circ$).

The ethyl ester reacts with phosphorus pentabromide, yielding the bromethyl ester, which was isolated as an oil boiling at 165° – 170° (20 m.m.). This was treated with diethylaniline, and the unsaturated ethyl ester, boiling at 155° (10 m.m.) hydrolysed, when an acid was obtained

which boiled at 180–200° (10 m.m.), and answered Baeyer's test for an unsaturated acid. It was now oxidised, first with cold permanganate, and then with chromic acid, to an acid which was proved by analysis of the crystalline silver salt to be isobutyric acid.

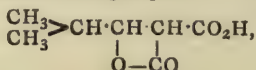
The probable formula for the lactonic acid is therefore—



Action of Methyl Iodide on Isopilocarpine.—When isopilocarpine methiodide is heated with potash solution in a sealed tube, the base formed is methylamine, thus proving that the nitrogen atom to which pilocarpine owes its basic character is the one eliminated in various reactions as ammonia. By treatment with silver hydroxide and subsequent heating, a new base is formed—*methylisopilocarpine*—which is insoluble in chloroform and forms a crystalline platinichloride, m. p. 218°, and a crystalline picrate, m. p. 136°. This base reacts with methyl iodide to form a methiodide, from which, however, by treatment with silver hydroxide, the original base—methylisopilocarpine is obtained. It was not found possible to introduce more than one methyl group. Methylisopilocarpine methiodide, on heating with potash solution in a sealed tube, yields only one base—methylamine. These experiments prove the existence of the group :NH in isopilocarpine, and, since the other nitrogen atom always yields methylamine, it must occur as the group :NCH₃. Herzig and Meyer have stated that one methyl group is attached to a nitrogen atom, and Chastaing was unable to prepare dialkyl derivatives.

Without proposing any formula for isopilocarpine, it may be desirable to state the facts which any formula for the base must explain:—

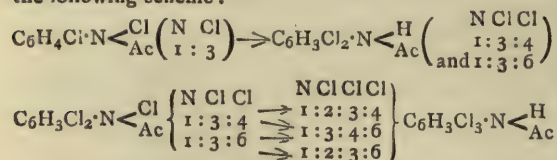
1. The optical behaviour of pilocarpine and isopilocarpine, and the remarkable stability of the latter base towards heat, alkalis, and various chemical reagents.
2. The non-basic character of the group :NCH₃.
3. The existence of the groups—



:NH, and :NCH₃.

*78. "The Nitrogen Chlorides derivable from Meta-chloro-acetanilide and their Transformations." By F. D. CHATTAWAY, K. J. P. ORTON, and W. H. HURTLEY.

The action of hypochlorous acid on meta-chloro-acetanilide was described. The nitrogen chlorides formed, and the transformations they undergo, are represented by the following scheme:—



Each of the three tri-chloro-acetanilides yields nitrogen chlorides, which change into the same tetra-chloro-acetanilide (NH : Cl : Cl : Cl : Cl = 1 : 2 : 3 : 4 : 6). In the transformation of these nitrogen chlorides in which one meta-position is occupied, the formation of the ortho-derivatives takes place to a greater extent than in the transformation of the nitrogen chlorides derived from acetanilide (*Proc.*, 1900, xvi., 112). The transformation is also a much slower and more difficult process.

The following substances are described:—

Metachlorophenylacetylnitrogen chloride (acetylchloramino-3-chlorobenzene), C₆H₄Cl·NCl·COCH₃. Clusters of small prisms, m. p. 93°.

3:4-Dichlorophenylacetylnitrogen chloride (acetylchloramino 3:4-dichlorobenzene), C₆H₃Cl₂·NCl·COCH₃. Clusters of very slender prisms, m. p. 92°.

2:5-Dichlorophenylacetylnitrogen chloride (acetylchloramino-2:5-dichlorobenzene), C₆H₃Cl₂·NCl·COCH₃. Small prisms, m. p. 73°.

2:3:4-Trichlorophenylacetylnitrogen chloride (acetylchloramino-2:3:4-trichlorobenzene), C₆H₂Cl₃·NCl·COCH₃. Clusters of flattened prisms, m. p. 113–114°.

2:4:5-Trichlorophenylacetylnitrogen chloride (acetylchloramino-2:4:5-trichlorobenzene), C₆H₂Cl₃·NCl·COCH₃. Rosettes of short, thick prisms, m. p. 96°.

2:3:6-Trichlorophenylacetylnitrogen chloride (acetylchloramino 2:3:6-trichlorobenzene), C₆H₂Cl₃·NCl·COCH₃. Small, four-sided prisms or plates, m. p. 116°.

2:3:4:6-Tetrachlorophenylacetylnitrogen chloride (acetylchloramino - 2:3:4:6-tetrachlorobenzene), C₆H₂Cl₄·NCl·COCH₃. Clusters of small prisms, m. p. 97°.

*79. "The Persulphuric Acids." By T. MARTIN LOWRY, D.Sc., and JOHN H. WEST.

This work was undertaken in order to elucidate the part which "persulphuric acid" plays in the accumulator (Armstrong and Robertson, *Proc. Roy. Soc.*, 1891, I., 105) and to ascertain to what extent the production of this acid must be taken into account in discussing the electric conductivity of solutions of sulphuric acid, as well as in determining the origin of the products which such solutions yield when electrolysed under various conditions (Armstrong, *Trans.*, 1895, lxvii., 1156).

In the course of the inquiry it became necessary to repeat and extend Berthelot's observations on the interaction of hydrogen peroxide and sulphuric acid (*Ann. Chim. Phys.*, 1878, [v.], xiv., 345–354). The experiments have led to results which appear to have an important bearing on the constitution of the product formed by the interaction of sulphuric acid and potassium persulphate which Caro (*Zeit. Ang. Ch.*, 1898, iv., 845) has shown to be possessed of special properties, and which Bamberger as well as v. Baeyer and Villiger have made use of as an characterised by Caro is a "persulphuric" acid composed oxidising agent under the name of "Caro's reagent." It has been suggested by v. Baeyer and Villiger that the acid of hydrogen peroxide and sulphuric anhydride in the ratio H₂O₂:SO₃. The author's experiments favour the conclusion that its composition may be H₂O₂:4SO₃; the acid of which salts were first prepared by Marshall, being of intermediate composition—H₂O₂:2SO₃. The members of such a series of persulphuric acids may be provisionally distinguished as "persulphuric," "perdisulphuric," and "pertetrasulphuric acids."

Evidence of the composition of the acid in question has been obtained by determining the equilibrium which results on mixing solutions of sulphuric acid and hydrogen peroxide in various proportions. Over fifty different mixtures have been examined, and it has been found that the variation of equilibrium as the concentration changes can be represented by an equation of the type—

$$\frac{c_1}{c_2} = k_1 \left(\frac{c_3}{c_4} \right)^2 + k_2 \left(\frac{c_3}{c_4} \right)^4$$

where c_1 and c_2 are the relative molecular concentrations of the "persulphuric" acid and hydrogen peroxide, whilst c_3 and c_4 are the relative molecular proportions of sulphuric acid and water in the mixture. The peroxidation is effected almost entirely within the limits H₂SO₄ and H₂SO₄.5H₂O. The results indicate that in addition to the "pertetrasulphuric" acid, a small but increasing proportion of "perdisulphuric" acid is formed as the concentration decreases, and qualitative tests made in accordance with Caro's directions leave no doubt that this is the case.

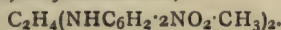
80. "On Diphenyl- and Dialkyl-ethylenediamines, their Nitro-derivatives, Nitrates, and Mercurichlorides." By W. S. MILLS, B.A.

When diphenylethylenediamine dissolved in glacial acetic acid is nitrated, a yellow precipitate is obtained towards the completion of the nitration. Purified from nitrobenzene, it melts at 307–303°, and is the tetranitro-

diphenylethylenediamine, $C_2H_4(NHC_6H_3(NO_2)_2)_2$ of Jedlicka (*Journ. Prakt. Chem.*, 1893, [ii.], xlviii., 202), prepared by the interaction of 2:4 bromodinitrobenzene and ethylenediamine.

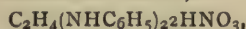
Water added to the solution from which the last-mentioned compound has separated precipitates a yellow amorphous powder, very soluble in acetone, ethyl acetate, and acetic acid. It melts at 85° , and is an isomeric tetra-nitrodiphenylethylenediamine, which, when boiled with acetone, is converted into Jedlicka's isomeride.

Diorthotolylethylenediamine nitrated in a similar manner gives a solution from which water precipitates a yellow amorphous powder, which melts at $78-79^\circ$; it is a tetra-nitrodiorthotolylethylenediamine,—



When heated with ethyl acetate, this compound undergoes a change similar to that observed in the case of its phenyl homologue, a yellow powder being obtained which melts at $178-180^\circ$, and is probably an isomeric tetra-nitro-diorthotolylethylenediamine. Dimetatolylethylenediamine on nitration gives a yellow powder very soluble in acetic acid, melting at 57° , and is tetranitrometatolylethylenediamine. Partial nitration of diparatolylethylenediamine gives a mass of fine orange-red crystals. This is dinitro-diparatolylethylenediamine, $C_2H_4(NHC_6H_3 \cdot NO_2 \cdot CH_3)_2$, melting at $195-196^\circ$ and is identical with that prepared by Gattermann and Hager (*Ber.*, 1884, xvii., 778) by the interaction of ethylene dibromide and metanitroparatoluidine.

Diphenylethylenediamine nitrate,—

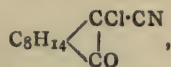


consists of needle-shaped crystals, m. p. 164.5° . Diorthotolylethylenediamine nitrate, $C_2H_4(NHC_6H_4CH_3)_2 \cdot 2HNO_3$, needles, m. p. 152° . Diparatolylethylenediamine nitrate, needles, m. p. 166.5° . Dimetatolylethylenediamine nitrate, needles, m. p. 153° .

The mercurichlorides are prepared by adding alcoholic solutions of mercuric chloride to alcoholic solutions of the bases in molecular proportions, when crystalline precipitates separate slowly on standing, except in the case of the metatolyl compound, which is obtained by spontaneous evaporation of the mixed solutions. Diphenylethylenediamine-mercurichloride, $C_2H_4(NHC_6H_5)_2 \cdot HgCl_2$, well-formed rhombic plates, m. p. 129° ; Diorthotolylethylenediamine-mercurichloride, small rhombic plates, m. p. 110° ; Diparatolylethylenediamine mercurichloride, in white feathery flakes, m. p. 133° . Dimetatolylethylenediamine mercurichloride, rosettes needles, m. p. $79-80^\circ$.

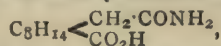
81. "Derivatives of Cyanocamphor and Homocamphoric Acid." By ARTHUR LAPWORTH.

Cyanocamphor is easily obtained in large quantities by a modification of the method of Bishop, Claisen, and Sinclair (*Annalen*, 1894, cclxxi., 351). Chlorocyanocamphor,—



crystallises in brilliant prisms melting at $98-100^\circ$. Cyanocamphor and its bromo- and chloro-derivatives are dimorphous.

When the halogen derivatives of cyanocamphor are heated with strong aqueous alkalis, reduction occurs, and cyanocamphor and homocamphoric acid—



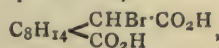
are produced. The latter crystallises in large prisms which melt and decompose at $209-210^\circ$.

Homocamphoric acid crystallises well from nitrobenzene, forming beautiful white needles which are apparently uniaxial.

When homocamphoric acid is heated with bromine in a sealed tube, action occurs at 140° , but much more than a molecular proportion of bromine is used up, and the

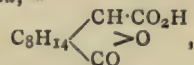
products are difficult to isolate. When it is brominated in presence of phosphorus pentabromide and the product is treated with alcohol, diethylaniline, and alcoholic potash successively, a lactone, $C_{10}H_{16}O_2$, is obtained; this is volatile with steam, and crystallises in colourless needles melting at 146° .

a Bromohomocamphoric acid,—



is made by heating the dichloride of homocamphoric acid with bromine on the water-bath. It separates from ethyl acetate in small, six-sided leaflets, and from benzene in slender needles. It melts sharply, under certain conditions, at $181-182^\circ$. Unlike all the allied substances, namely, camphoric acid and its halogen derivatives, and homocamphoric acid itself, it dissolves in chloroform and benzene.

When its diethyl ester is heated with diethyl aniline, it loses ethyl bromide, and gives the ethyl ester of homocamphoric acid,—



The same acid is obtained by warming an aqueous solution of sodium bromohomocamphoric acid; it crystallises in glistening needles or six-sided plates melting at $161-162^\circ$.

Experiments are being made with the object of preparing dehydrohomocamphoric acid,—



which should afford interesting results on oxidation.

(To be continued).

NOTICES OF BOOKS.

The Kinetic Theory of Gases. By Dr. OSKAR EMIL MEYER. Translated from the Second Edition, by ROBERT E. BAYNES, M.A. Pp. 472. London, New York, and Bombay: Longmans, Green, and Co.

DR. MEYER has made many additions to this work since its first appearance more than twenty years ago, though the general plan of the book remains the same.

The subject is treated in three parts, with six mathematical appendices; this arrangement facilitating the task of the ordinary reader who wishes to see how the several objections to the theory have been met, or attempted to be met; whilst for the chosen few who revel in mathematics, ample material has been provided at the end of the volume for the satisfaction of their appetites.

Part I treats of molecular motion and its energy, and in five chapters Dr. Meyer sets forth the history of the theory since its practical inception by Bernouilli in 1752, and its modern development by Clausius, Joule, and Maxwell, almost a century later. During the last half century, however, the range of conditions under which gases may be examined has been enormously increased, and from time to time objections have been raised against the theory as originally propounded, which have almost caused it to be finally rejected as untenable; but at the critical moment some one (chiefly German) has always arisen and proposed some slight modification of the original simple equations, taking account of some hitherto ignored factor, and once more reconciling theory with experimental results, until at the present day it rests upon hypotheses regarding the nature of ultimate matter, which, however they may appeal to the scientific imagination, seem for the present to be neither capable of being proved nor disproved.

As an illustration of the thorough manner in which

Dr. Meyer has explored his ground, it may be noted that in the chapter on "Maxwell's Law," which covers fifty pages of the text, there are no less than ninety-eight references to original publications bearing on the subject.

In Part 2, dealing with "Molecular Free Paths, and the Phenomena conditioned by them," fully as much progress has been made in the direction of a more searching enquiry into all the governing factors, with the result that many phenomena which, a quarter of a century ago, appeared to be at variance with theoretical requirements, have been recognised as agreeing with theory well within the limits of experimental error. The theory of the viscosity of gases is set forth with great clearness in Chapter 7, where the influence of partial or complete dissociation of a compound molecule on the viscosity is shown to fully account for the varying results obtained by different observers under different conditions.

In considering the theory of the conduction of heat, it should be noted that ethylene and nitrous oxide do not give nearly such good results as other gases, for in the tables on page 294 these gases show a difference of 10 per cent between the calculated and observed values, whilst air and carbonic acid show a difference of less than 1 per cent; it is only fair, however, to point out, as Dr. Meyer himself does, that the factors of the calculated figures are themselves approximations, and that "all differences between theory and observation might find their explanation in the accumulation of the errors of experiment."

Part 3, which deals with "The Direct Properties of Molecules," is much more speculative in character. In fact, as Dr. Meyer is careful to point out, many of the results arrived at may be accepted as not impossible rather than as probable.

When we consider, for instance, the several means by which the probable diameter of the "molecular sphere of influence" is calculated, each of which involves quantities that are only approximately known, it is a matter for surprise that Dorn, Loschmidt, van der Waals, and Meyer should have arrived at figures which lie within such close limits as $1/5$ th and 2 millionths of a millimetre, more especially since the larger figure is "a limit greater than which a molecule can not be."

The Mathematical Appendices, six in number, are of interest to those who can understand them, but do not appear to contain anything not previously published.

Physical Reactions and the "Mass Law." By AZARIAH T. LINCOLN. (Reprinted from the *Journal of Physical Chemistry*, vol. iv., No. 3, March, 1900).

AN interesting and useful contribution to our knowledge of a class of phenomena to which but little attention has been paid. Professor Bancroft in 1894 showed that the "Mass Law" could be applied to a class of conditions of equilibrium in which the exponential factors of the mathematical formula representing the equilibrium are not necessarily integers, and are usually not integers. This formula is empirical, and Mr. Lincoln has endeavoured to show by experiment that it is the mathematical expression of a new Law of Nature.

The ground to be covered is very wide and in general very complex. Mr. Lincoln has confined his experiments to one of the simplest class of phenomena, and, so far as he has gone, has succeeded in demonstrating the all but identity of the observed and calculated results.

The application of the mass law to the case of two non-miscible liquids and a consolute liquid is as follows:—If the amount of the consolute liquid be called " x " and the amounts of the non-miscible liquids " x " and " y ," then—

$$\frac{x^{\alpha}y^{\beta}}{x^{\alpha}+y^{\beta}} = C.$$

Or, $\alpha \log x + \beta \log y - (\alpha + \beta) \log z = \log C = C'.$

Mr. Lincoln has performed a series of most careful experiments with benzol, water, and alcohol in various proportions, and has found that the calculated and observed quantities of alcohol, "the unknown quantity," agree within one-third of one per cent, thus showing in a remarkable way both his own skill as an experimenter and the accuracy of the empirical formula as applied to the phenomena under investigation.

The Theory of Electrolytic Dissociation and some of its Applications. By HARRY C. JONES. London: Macmillan and Co., Lim. New York: The Macmillan Co. 1900. Pp. 289.

MANY students have found a difficulty in obtaining a comprehensive account of the newer developments in physical chemistry, such as the relation between osmotic pressure and gas pressure, the origin and significance of the theory of electrolytic dissociation, &c. Until the appearance of this volume much of this information could only be obtained from certain original papers, not always easy of access: the above-mentioned and other matters are now placed before the reader in a systematic manner.

The author divides his subject into four parts or chapters. Chap. I., on the earlier Physical Chemistry, comprises a study of the relations between properties and composition, and properties and constitution; the development of thermo-chemistry and electro-chemistry, chemical dynamics and chemical statics, from which can be seen not only the state of development, but also the inherent nature of physical chemistry. The aim of the physical chemist in early times was to connect, and thus systematise, the great masses of isolated facts, and refer them as far as possible to common causes.

Pfeffer's osmotic investigations next claim attention in Chapter II. The phenomenon of osmosis is the passage of a pure solvent through a partition, to join a solution of a substance on the other side, which substance is unable to pass through the partition itself; the pressure thus produced is called osmotic pressure.

Chapter III. deals with the evidence bearing upon the theory of electrolytic dissociation; the evidence in favour of this theory is so overwhelming, in comparison with the few apparent exceptions, that the author considers these latter should be examined very closely before concluding finally that they are real exceptions.

The fourth and last chapter is on some applications of the theory of electrolytic dissociation, or, in other words, showing what is the scientific use of this theory. A careful study of this chapter will bring out a fact of profound significance. The theory, it will be seen, co-ordinates and correlates heterogeneous masses of facts, which apparently bore little or no relation to each other, and refers them to a common cause. Physical chemistry, the author tells us in conclusion, is furnishing us by the aid of the theory of electrolytic dissociation, with rational explanations of chemical processes whose meaning was entirely concealed, and is rapidly placing chemistry upon that exact mathematical basis which physics has so long enjoyed.

Kelly's Directory of Chemists and Druggists. 1900. Ninth Edition. London: Kelly's Directories, Lim. Pp. 691.

In the pages of this Directory will be found the names of over 49,000 persons, being an increase, as compared with the last edition, of about 9000. These include not only chemists and druggists, as the title might imply, but also manufacturing chemists, dentists, veterinary surgeons, wholesale druggists, drysalts, mineral water manufacturers, photographers, &c. Another addition is, that the names for the Isle of Man and the Channel Islands are included for the first time.

CORRESPONDENCE.

DISTILLATION WITHOUT BUMPING.

To the Editor of the Chemical News.

SIR,—“A Ghost of 200 Years” appears to be acquainted with buried discoveries of the past; it would be more to the purpose if he could tell us whether the fact I stated were generally known now. The only suggestion that I have come across and acted upon more than once (with unsatisfactory results) is that of using freshly broken crystals of quartz (Miller, “Elements of Chemistry,” vol. ii., p. 202). The use, however, of broken fragments of common tobacco-pipe leaves nothing to be desired, and would certainly have been mentioned in preference if it had been known to him. Fresenius suggests no foreign body, and Crookes does not notice this under the above heading. Is it because its use is so very common? There are many little details of manipulation which we hit upon after years of practice, only because they are not recorded in our textbooks.—I am, &c.

G. F. M. FIELDING.

Staplehurst, June 18, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 21, May 21, 1900.

Formation of Nitric Acid during Combustions.—M. Berthelot.—The formation of small quantities of nitric acid—or, more precisely, oxides of nitrogen transformable into this acid—during the combustion of hydrogen or various hydrocarbons, has been observed by many chemists, but has never been the subject of a systematic study. The author has undertaken this investigation, utilising his numerous determinations of heats of combustion and formation of organic compounds. During these determinations, the small quantity of nitric acid was always determined by reason of the simultaneous oxidation of the nitrogen contained in the oxygen used.

Limits of Combustibility of Hydrogen and Gaseous Hydrocarbons Diluted with Large Volumes of Air by means of Copper Oxide at a Red Heat.—Armand Gautier.—Hydrogen and gaseous hydrocarbons, when passed over copper oxide at a red heat, are transformed into water and carbon dioxide, but this reaction is retarded to a certain extent by the products themselves as they are formed; and, in the case of hydrogen or the other combustible vapours being mixed beforehand with large volumes of inert gas, the question arises as to whether their combustion is total. The author's first experiments were tried with hydrogen mixed with five thousand times its volume of air, and passing over a column of red-hot copper oxide 70 c.m. long at the rate of 2 to 3 litres per hour, and he finds that the hydrogen is entirely burnt. In the case of methane, he finds that the quantity of methane which burns when passing over copper oxide, together with large quantities of air, diminishes with the dilution.

Action of Hydrobromic Acid on Dextro-benzylidene Camphor, Monobromo-benzyl Camphor, Dextro-benzylidene-campholic and Phenylxyhomo-campholic Acids.—A. Haller and J. Minguin.—When finely powdered dextro-benzylidene camphor is dissolved in crystalline acetic acid saturated with hydrobromic acid, and this is left standing in the cold for a month or six weeks, white crystals separate out, which have the formula

$C_8H_{14} \leftarrow \begin{smallmatrix} CH.CH.Br.C_6H_5 \\ CO \end{smallmatrix}$, and are called monobromo-benzyl camphor. Various properties and reactions of this substance are described in this paper.

Anhydrous Calcium Dioxide and the Constitution of its Hydrates.—M. de Forcrand.—The precipitate of hydrated calcium dioxide, $CaO_2 + 8H_2O$, has been already described by the author. This substance, when kept cool, can be dried in a vacuum by means of phosphoric anhydride. After six days, a dry amorphous powder was produced, which gave on analysis $CaO_{1.94} + 0.13H_2O$, or very nearly anhydrous CaO_2 . The author examines the various hydrates which this substance forms, and measures the heat of formation.

Some Properties of Aluminium, and the Preparation of Gaseous Hydrogen Phosphide.—Camille Matignon.—The author uses aluminium phosphide for the preparation of hydrogen phosphide. The aluminium phosphide is placed with water in a flask, the cork being fitted with a dropping funnel containing sulphuric acid. Water attacks the phosphide at ordinary temperatures, but traces of acid accelerate this decomposition. By means of the dropping funnel the action can be regulated. The gas produced by this means is extremely pure. The actions of sulphur, selenium, phosphorus, arsenic, and antimony on aluminium powder are of explosive violence, and are strongly exothermic. This method of direct preparation is, however, very rapid and easy.

Compounds of Lithium Bromide with Ammonia Gas.—J. Bonnefoi.—In the same manner as lithium chloride, lithium bromide, when absolutely pure and dry, absorbs ammonia gas, and forms with it four compounds which are extremely deliquescent, $LiBr \cdot NH_3$, $LiBr \cdot 2NH_3$, $LiBr \cdot 3NH_3$, and $LiBr \cdot 4NH_3$. The four molecules of ammonia successively added to $LiBr$ evolve:—First molecule, +13.293; second molecule, +12.644; third molecule, +11.526; fourth molecule, +10.635; making a total of +48.098 calories, numbers in each case greater than the corresponding numbers for $LiCl$.

Two Polysulphides of Lead and Copper.—F. Bodroux.—When polysulphide of calcium is poured into a dilute solution of a lead or copper salt, a voluminous precipitate is produced, whose colour varies with the nature of the metal. The author isolates these two bodies, and shows by analysis that they have the composition PbS_2 and Cu_2S_2 respectively. PbS_2 is a purplish red substance at a low temperature. Above 10° it rapidly decomposes into lead monosulphide and sulphur. Cu_2S_2 is a brownish red body, stable at ordinary temperatures, but decomposing after some days into the monosulphide and sulphur.

A Chlorosulphide of Mercury.—F. Bodroux.—When calcium polysulphide acts on excess of a solid saturated solution of mercuric chloride, a totally different action takes place from those described in the previous papers. A yellow precipitate is formed, whose colour gradually fades. When dried, it is a white powder. Analysis shows this substance to have the formula $Hg_2S_5 \cdot HgCl_2$. This chlorosulphide is very stable at ordinary temperatures, but superficially alters on prolonged exposure to light. It is insoluble in the alkaline sulphides and the alkalis, which blacken whilst decomposing it.

Action of Water on Mercurous Sulphate.—M. Gouy.—The author investigates the decomposition of mercurous sulphate by means of water, and the formation of basic mercurous sulphate.

Partial Synthesis of Lævo-erythrite.—L. Maquenne.—This preliminary notice contains an account of various new compounds which the author obtained in the course of the synthesis of lævo-erythrite: xylosoxime, acetyl-xylic nitrile, *l*-erythrose-acetamide, and, finally, *l*-erythrite.

Preparation of the Dialcylamidodichlor-anthraquinones.—E. C. Severin.—It appears that the presence

of two atoms of chlorine with regard to one of the carboxyl groups prevents the condensation of the dichlorodialcylamidobenzoylbenzoic acid, and is only effectual when operating on the benzyl acids, and under other conditions than those described by MM. Haller and Guyot.

Monoiodohydrine of Glycol.—E. Charon and M. Paix-Séailles.

γ -Chlorocrotonic Acid.—R. Lespieau.

MISCELLANEOUS.

Society of Arts Medals.—The Council have awarded the Society's Silver Medal to the following readers of papers during the Session 1899-1900:—

To D. E. HUTCHINS, Conservator of Forests, Cape Town, for his paper on "National Forestry."

To Sir W. MARTIN CONWAY, M.A., for his paper on "Some of the Undeveloped Resources of Bolivia."

To EDMUND WILSON, for his paper on "The Housing of the Poor."

To Professor R. W. WOOD, for his paper on "The Diffraction Process of Colour Photography."

To EDWIN BALE, R.I., for his paper on "Artistic Copyright."

To Miss HALSEY, for her paper on "Some Unfamiliar Masterpieces of the Italian School."

To Professor W. M. FLINDERS PETRIE, D.C.L., for his paper on "A National Repository of Science and Art."

To A. R. COLQUHOUN, for his paper on "Russia, Persia, and Afghanistan."

To Sir WILLIAM LEE-WARNER, K.C.S.I., M.A., for his paper on "Our Work in India in the 19th Century."

To CHRISTOPHER RAWSON, F.I.C., for his paper on "The Cultivation, Manufacture, and Use of Indigo—Position of the Industry in India."

To JOHN FERGUSON, for his paper on "Old and New Colombo."

To the Right Hon. Sir CHARLES WENTWORTH DILKE, Bart., M.P., for his paper on "The Century in Our Colonies."

To CYRIL DAVENPORT, for his paper on "Niello Work."

To LASENBY LIBERTY, for his paper on "English Furniture."

The Society of Arts Albert Medal for the present year has, with the approval of His Royal Highness the Prince of Wales, President of the Society, been awarded to Mr. Henry Wilde, F.R.S., "for the discovery and practical demonstration of the indefinite increase of the magnetic and electric forces from quantities indefinitely small." This principle is the one on which the invention of the modern dynamo machine is based, and is employed in all modern dynamos.

Action of Hypochlorous and Hypobromous Acids on Acetylene, and on the Mono-substituted Acetylenes.—N. Vittori.—Acetylene does not unite with HClO up to 50° , but it unites with 2HBrO , forming dibromoacetic aldehyde, CHBr_2CHO : this latter gives, besides the known monohydrate, a stable crystallised dihydrate. These hydrates, the same as the aldehyde, give glyoxime by means of the chlorhydrate of hydroxylamine. The union of allylene with HClO or with HBrO produces a dichlorised or dibromised ketone, which is transformed into methylglyoxime by the chlorhydrate of hydroxylamine. By the combination of HClO or HBrO with trimethylallylene, we obtain the dichlorised or dibromised pinacolines, the first fusible at 51° and the second at $75^\circ-75.5^\circ$. With phenyl-acetylene HClO gives dichloroacetophenone, fusible at $19^\circ-20^\circ$, which furnishes a dioxime fusible at $156^\circ-158^\circ$.—*Journ. Soc. Phys. Chim. R.*, xxxi., p. 490.

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THE CHEMICAL NEWS.

VOL. LXXXI., No. 2118.

THE NATURE AND ORIGIN OF THE POISON OF LOTUS ARABICUS.*

By WYNDHAM R. DUNSTAN, M.A., F.R.S., Sec.C.S.,
Director of the Scientific Department of the Imperial Institute,
and
T. A. HENRY, B.Sc., Lond.

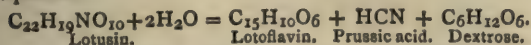
Lotus Arabicus is a small leguminous plant resembling a vetch, indigenous to Egypt and Northern Africa. It grows abundantly in Nubia, and is especially noticeable in the bed of the Nile from Luxor to Wady Halfa. It is known to the natives as "Khuther," and old plants with ripe seed are used as fodder. At certain stages of its growth it is highly poisonous to horses, sheep, and goats, the poisonous property being most marked in the young plant up to the period of seeding. Owing to the trouble which this plant has given to the military and civil authorities in Egypt, the assistance of the Director of Kew was sought in order that the precise nature of the poison might be ascertained, and, if possible, a remedy found. The matter having been referred to the Scientific Department of the Imperial Institute, Mr. E. A. Floyer, Director of Egyptian Telegraphs, collected some of the material for investigation. The dried plant is unusually green, and possesses the aroma of new-mown hay.

It was found that when moistened with water and crushed, the leaves of the plant evolved prussic acid in considerable quantity, the amount being greatest in the plant just before and least just after the flowering period. Further investigation has shown that the prussic acid originates with a yellow crystalline glucoside ($C_{22}H_{19}NO_{10}$), which it is proposed to name *lotusin*. Under the influence of an enzyme, also contained in the plant, lotusin is rapidly hydrolysed, forming *prussic acid*, *sugar*, and a new yellow colouring matter (*lotoflavin*). The hydrolysis may be effected by dilute acids, but it is only very slowly brought about by emulsin and not at all by diastase. The peculiar enzyme, which it is proposed to call *lotase*, appears to be distinct from the enzymes already known. Its activity is rapidly abolished by contact with alcohol, and it has only a feeble action on amygdalin. Old plants are found to contain lotase but no lotusin.

The *sugar* has been proved to be identical with ordinary dextrose.

Lotoflavin, the yellow colouring matter, has the composition expressed by the formula $C_{15}H_{10}O_6$. It belongs to the class of phenylated pheno- γ -pyrones, and is a dihydroxychrysin, isomeric with luteolin, the yellow colouring matter of *Reseda luteola*, and with fisetin in the yellow colouring matter of *Rhus cotinus*.

The decomposition which ensues on bringing lotase in contact with lotusin, as happens when the plant is crushed with water, is therefore probably expressed by the following equation:—



Hydrocyanic (prussic) acid occurs in small quantity in many plants, and according to Treub and Greshof is often present in the free state. The only glucoside at present definitely known which furnishes this acid is the well-known amygdalin of bitter almonds, which under the influence of the enzyme emulsin, also contained in the almond, breaks up into dextrose, benzaldehyde, and prussic acid.

Owing to the scientific interest which attaches to this new glucoside, its properties and those of its decomposition products have been very fully studied, and the characteristics of the new enzyme have also been investigated.

We are much indebted to Mr. Floyer for the great pains he has taken to collect, in Nubia, the necessary material for this investigation, and also to Sir W. T. Thielton-Dyer for having grown the plant at Kew, from seed obtained from Egypt.

ON THE EXISTENCE OF THERMAL CENTRES OF STABILITY IN COMPOUNDS.

By GEOFFREY MARTIN.

ALL chemical combinations may be divided into two great classes—endothermic and exothermic.

In endothermic compounds the atoms are held together in such a way that energy is stored up in the molecule. Consequently, when the molecule is decomposed, this stored-up energy is liberated, principally in the form of heat. Endothermic compounds are usually explosive, and for the reason that, in separating the atoms of the molecule, work is done *with* not *against* the internal atomic forces.

In exothermic compounds, however, the contrary is the case, and the coming together of the atoms which compose them is attended with the evolution of energy. In order to decompose such a molecule, work must be done *against* the atomic forces within the molecule. Such compounds are therefore usually stable.

The heat of formation of a compound may be either positive or negative, according as it is exothermic or endothermic. Now, it is well known that the heat of formation of a compound is not a constant, but varies with the temperature. In a great many cases it diminishes with the increasing temperature. This may also be directly deduced from the kinetic theory of matter (in the case of exothermic compounds at least), for the higher the temperature the greater the internal atomic motion within the molecule, consequently the more feebly are the atoms held together. But the force with which the atoms are held together must be some function of the absolute heat of formation of that compound; and, consequently, we should expect that, in the case of an exothermic compound, an increase in temperature should lead to a diminution in its heat of formation.

This reasoning assumes that the fundamental attraction of the atoms for each other is a constant—an assumption that is by no means warranted by the facts, as will be seen later.

The dependence of the heat of formation upon the temperature has been investigated in the case of very few endothermic compounds. Victor Meyer, however, in 1893, studied the case of hydrogen iodide. The heat of formation of this compound is -6100 calories. With increase of temperature, the negative value of its heat of formation continually diminishes until, at $324^\circ C$, it becomes zero. At still higher temperatures it becomes positive. In this case, then, we have an example of an endothermic compound gradually changing into an exothermic compound. Suppose, now, we heated an exothermic compound beyond the temperature at which its heat of formation is zero, would it conversely become an endothermic compound? I shall bring forward some indirect evidence later tending to show that, if this be so, we have the key wherewith to explain some very remarkable phenomena.

I fail to perceive the necessity of drawing an arbitrary distinction between endothermic and exothermic compounds. I would regard them as only the different stages of the physical alteration of a compound with the temperature. The fact that a compound is at ordinary temperatures endothermic or exothermic, as the case may be,

* Abstract of a Paper read before the Royal Society, June 14, 1900.

is, according to my way of looking at the matter, a mere accident of the temperature. A compound probably passes successively with the temperature from an endothermic to an exothermic state, and—at still higher temperatures—back again into the endothermic state. According to this view, the positive or negative value of heat of formation of a compound is a periodic or recurring function of the temperature. Of course, the body need not necessarily be regarded as capable of existing undissociated throughout all these changes of temperature.

According to the modern theory of chemistry, the dissociation of a compound is a reversible chemical reaction. If, therefore, we assume that the positive or negative value of the heat of formation of certain compounds is a periodic or recurring function of the temperature, we can apply the laws of thermodynamics to investigate in what manner the dissociation will vary with the temperature.

Consider the gaseous reaction—



where A and B are molecular species which, by reacting on each other, give rise to the molecular species A' and B'. Then, according to the law of mass action, the velocity of the change from the left to the right, in the sense of the above equation, is—

$$v = k \cdot c_1 c_2 \quad \dots \dots \dots (1).$$

where c_1 and c_2 are the active masses of the reacting molecules A and B respectively, and k is the proportional constant. Similarly, the velocity of the reaction in the sense of the equation from the right to the left is—

$$v_1 = k' \cdot c_1' c_2' \quad \dots \dots \dots (2).$$

But when a state of equilibrium has been arrived at—

$$v = v_1$$

or—

$$k c_1 c_2 = k' c_1' c_2',$$

denote—

$$\frac{k}{k'} \text{ by } K.$$

Then—

$$K = \frac{c_1' c_2'}{c_1 c_2} \quad \dots \dots \dots (3).$$

K is the coefficient of equilibrium of the system, and it denotes how much faster the reaction proceeds in the sense of the above equation from the left to the right than from the right to the left.

This coefficient K varies with the temperature. This variation at constant volume is expressed by the equation derived from thermodynamical considerations by van't Hoff—

$$\frac{d \log K}{dT} = \frac{q}{R T^2} \quad \dots \dots \dots (4).$$

T denotes the absolute temperature of the system, while R is the ordinary gas constant in the equation $p v = RT$ expressed in suitable units. It is advisable to thoroughly understand the nature of q . q denotes the total internal change in the energy of the system in consequence of the reaction.

If the molecular species A and B when reacting to produce A' and B' evolve heat, then the products of the change (A' and B') possess less internal energy than the molecular species whence they are derived, namely, A and B. q is in this case associated with a diminution in the total internal energy of the whole system, and consequently is negative. If, however, the products A' and B' are produced from A and B with the absorption of heat, then the products A' and B' are at a higher energy potential than A and B; consequently, the reaction $A + B = A' + B'$ is associated with an increase in the total internal energy of the system, and it follows that q is positive. To sum up then, q is negative in the case of an exothermic reaction, and positive in the case of an endothermic reaction.

Re-arranging Equation 4 we obtain—

$$d \log K = \frac{q}{R} \cdot \frac{dT}{T^2},$$

integrating—

$$\log K = -\frac{q}{R} \cdot \frac{1}{T} + \text{constant}.$$

Let K_1 and K_2 represent the equilibrium coefficients of the system at two different temperatures T_1 and T_2 ($T_2 > T_1$). Further, suppose T_2 and T_1 to be close together, so that q will not change noticeably between the interval T_2 and T_1 . Then, substituting these values in the above equation and subtracting, we obtain—

$$\log K_2 - \log K_1 = \frac{q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (5).$$

Now, according to our hypothesis, q successively changes from a positive value (say) through zero to a negative value.

So long as q has a finite positive value, the expression $\log K_2 - \log K_1$ has also a positive value. Hence—

$$K_2 > K_1$$

so long as the value of the equilibrium coefficient increases with the increasing temperature—although at a diminishing rate, as may be seen from the form of Equation 5. But K represents how much faster the system $A + B$ reacts to produce A' + B' than the system A' + B' reacts to reproduce A + B.

Consequently an increase in the value of K means that there occurs in the gaseous mixture we are considering a decrease in the amount of A + B and an increase in the amount of A' + B' present per unit volume. Consequently, with rise of temperature, q remaining positive, the reaction—



tends more and more to cause the complete conversion of the A and B molecular species into the A' and B' species. Hence in those cases of dissociation which are attended by an absorption of heat—such as the dissociation of CaCO_3 , N_2O_4 , &c.—the dissociation becomes more and more complete as the temperature increases.

When, however, $q = 0$,

$$K_2 = K_1,$$

and so long as q retains this value a further increase of temperature does not cause the relative amounts of the species A and B, A' and B', in the system to vary.

But if q becomes negative, i.e., if the reaction $A + B = A' + B'$ is attended with the evolution of heat, as is the case when hydrogen and oxygen are heated together to a suitable temperature, then—

$$\log K_2 - \log K_1 = \text{a negative quantity}.$$

That is—

$$K_2 < K_1.$$

Hence with increasing temperature the system $A + B$ reacts to produce A' + B' at a slower rate than the system A' + B' reacts to reproduce the system A + B.

Consequently, with increase of temperature the amount of the molecular species A and B in the system continually increases at the expense of the A' and B' molecular species.

We thus arrive at the following law, which is known as van't Hoff's Principle of Mobile Equilibrium:—

If we heat a chemical system at constant volume, then there occurs a displacement of the state of equilibrium, and in that direction towards which the reaction advances with the absorption of heat.

Assuming the truth of the supposition that the heat of formation of compounds is a periodic or recurring function of the temperature, we may draw such a hypothetical curve representing this variation in the value of q as is shown in Fig. 1.

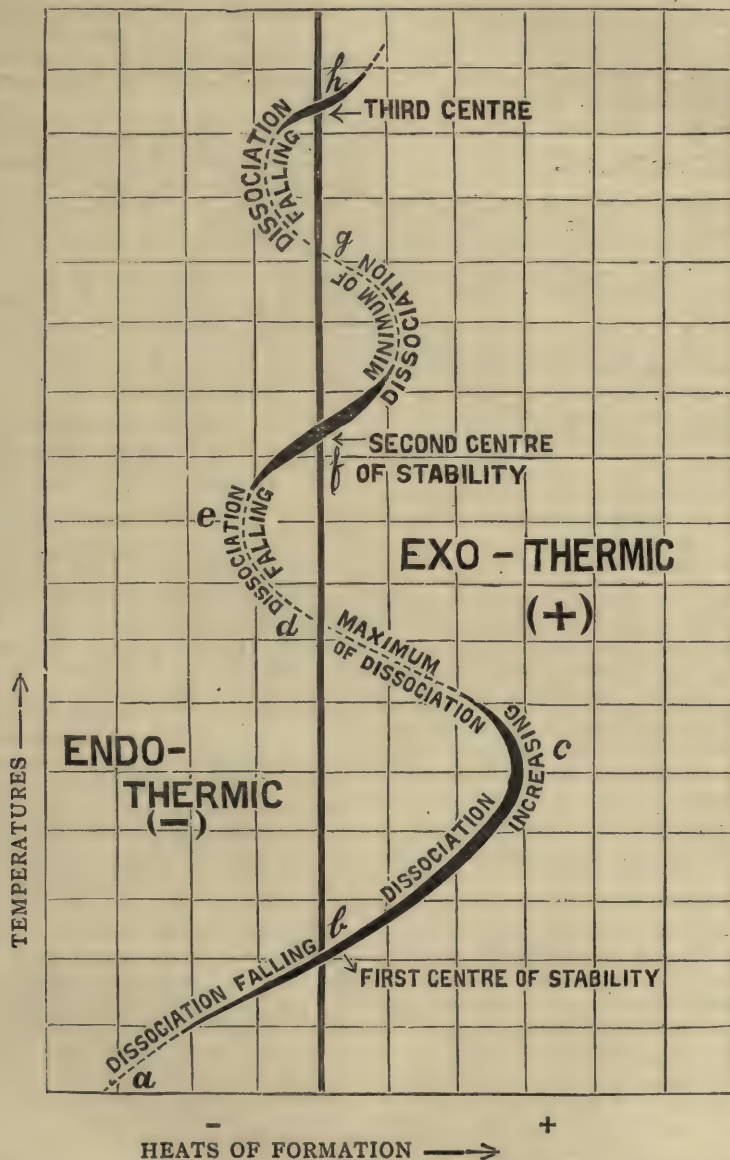
The abscissæ represents the heats of formation of the compound, and the ordinates the temperature.

On applying van 't Hoff's "Law of Mobile Equilibrium," we deduce that from *a* to *b* the dissociation of the compound continually retreats. At the point *b*, where the heat of formation is zero, a point of minimum dissociation occurs. This point is therefore the first centre of stability of the compound.

On further increasing the temperature the dissociation will continually increase, and the compound becomes exothermic. But it will be noticed that there are now

gas. On further heating, however, the heat of formation gradually diminishes, and consequently the increased motion of the atoms causes an increase in the amount of dissociation, which increases continually from (say) *c* to *d*, and attains a maximum at *d*. In many cases the body is completely decomposed at *d*; for example, silicon hexchloride.

At *d* the heat of formation again becomes zero, and further heating causes *q* to become negative. Conse-



two opposing forces at work. From *b* to *c* the compound becomes more and more exothermic, and consequently more and more stable. Nevertheless, with the increase of temperature, the motion of the atoms in the molecule becomes more pronounced. Usually the increased attraction of the atoms for each other is greater than their tendency to fly apart, and consequently from *b* to *c* the dissociation in many cases becomes practically negligible. Examples of such stable gases are ammonia and hydrochloric acid

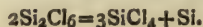
quently there is now a tendency for the atoms to aggregate together again, and this tendency increases continually with the temperature until the point *f* is reached. At *f* the dissociation will again be a minimum, and there will result a second "centre of stability" of the compound. By following up the curve we obtain a third centre of stability at *h*.

Of course one can hardly expect a gaseous body to exist all along the curve. In most cases it would probably only

be capable of existing at certain points. The dotted part of the curve shows when the body would be most liable to be incapable of existing.

In all cases, however, we should look for the substance to appear at the points *b*, *f*, and *h*, which we will call the first, second, and third centres of stability of the compound. On searching for experimental evidence of the existence of these points, I have collected at least six instances. Under this heading, of course, I include recurrent chemical reactions.

1. *The case of Silicon Hexchloride*, Si_2Cl_6 .—This substance is a colourless volatile liquid, which boils at 146°C . without decomposition. At 350°C . the vapour commences to dissociate, and the amount of dissociation continually increases up to 800°C ., when the compound is completely resolved into silicon and the tetrachloride, thus:—



Troost and Hautefeuille found, however, that if the temperature be quickly raised above 1000°C . that no dissociation occurred. The substance, therefore, is stable above 1000°C . and below 350°C ., but yet is incapable of existing at intermediate temperatures (*vide* Roscoe and Schorlemmer's "Chemistry").

2. *Hydrazine Hydrate*, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$.—This substance is a strongly refractive fuming liquid, which possesses extremely active chemical properties. It boils, unaltered, at 118.5°C . under 739.5 m.m. pressure, and its vapour at 100°C . has, under diminished pressure, a density corresponding to the formula $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. At 170°C . this vapour is completely dissociated into N_2H_4 and H_2O . At still higher temperatures the vapour density again continually increases, until finally it corresponds to a formula double that observed at 100°C . (*vide* Roscoe and Schorlemmer's "Chemistry").

3. *Ozone*, O_3 .—This compound is at ordinary temperatures very unstable, and is completely decomposed into oxygen gas at 250°C . Nevertheless Dewar showed ("Roy. Instit. Year Book," 1887-89, p. 559) that it could be produced at a white heat. His method was to heat up a platinum cylinder to a white heat, and pass a stream of oxygen gas through the tube. The oxygen gas thus heated was suddenly withdrawn and cooled by being sucked down by a stream of cold water circulating in an interior platinum tube. The resultant gas is said to have contained a large amount of ozone. From this experiment Dewar concludes that ozone has two centres of stability, and one of these is near the melting-point of platinum.

4. *Hydrogen Selenide*, H_2Se .—This was investigated by Ditte in 1872 (*Comptes Rendus*). He showed that its dissociation first increased, then diminished until a minimum was reached, and then again increased.

5. According to Ostwald ("Outlines of General Chemistry," p. 312, 1890 ed.) cyanogen and acetylene are other examples. Both gases are formed in quantity at the highest temperature we can produce—in the electric arc and in the blast furnace. Yet at a red heat these gases cannot exist, cyanogen, as is well known, falling apart into its elements, whilst acetylene decomposes into other and more stable hydrocarbons, such as benzene.

6. Victor Meyer and Langer have shown that chlorine violently attacks platinum at a low temperature, but is without action upon it between the range 300° — 1300°C . It then again begins to attack the platinum, the attack becoming violent between 1600° — 1700°C . ("Brit. Assoc. Reports," 1885, p. 961).

These cases, be it noticed, were all discovered by accident. No systematic search has, so far as I am aware, been specially made to discover other examples of recurrent chemical changes.

An analogous phenomenon is presented by certain cases of electrolytic dissociation. Thus, phosphoric and hypophosphoric acids at the temperatures 54° and 75°C . respectively show *maxima of conductivity*. Above these temperatures they have negative temperature coefficients.

It was Arrhenius who first discovered such electrolytes, and they are commonly regarded as anomalous. I would suggest, however, that they are but examples of a much wider law, and that probably under different physical conditions all compounds would exhibit analogous variations.

It must not be forgotten that hydrogen gas was once regarded anomalous in respect to its behaviour under pressure. But the subsequent researches of Amagat showed that under suitable physical conditions all the other permanent gases behaved similarly.

By glancing at the curve shown in Fig. 1, it will be seen that the smaller the maximum heat of formation of a compound is, the closer together will be the centres of stability.

In order, therefore, to experimentally investigate the recurring existence of compounds (or chemical reactions) at high temperatures, it would be well to choose bodies having small heats of formation.

Let not the significance of the above be missed. If there really exist thermal centres of stability, this proves that the attraction of the atoms for each other is not a constant, but depends upon their degree of relative motion; and, further, that this alteration in the attraction is a periodic function of the motion of the atoms.

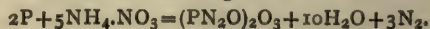
I intend shortly to make an extensive research on the behaviour of bodies at very high temperatures.

Merchant Venturers' College, Bristol,
May 16th, 1900.

ON THE ALLEGED TRANSFORMATION OF PHOSPHORUS INTO ARSENIC.

By CLEMENS WINKLER.

IN the March number of *Leopoldina*, No. 36, iii., page 40, F. Fittica seriously asserts that he has succeeded in partly transforming amorphous phosphorus into arsenic by heating it with ammonium nitrate to a temperature of, at most, 200° . He comes to the conclusion that arsenic is a nitrogen-oxygen compound of phosphorus, of the formula PN_2O , and that the "synthesis" takes place in accordance with the following formula:—



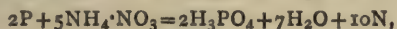
The assertion is not feasible. Arsenic has been obtained technically, especially in the form of its compounds, for at least 1000 years, and has been transformed on a very large scale from one form of combination into another in manufacturing operations without the least sign having hitherto been obtained which might justify any doubt of its elementary nature. There can be no question whatever that arsenic is really an element in the modern sense, a substance which cannot be decomposed into unequal constituents, and which cannot be composed from other elements. Fittica's assertion is based upon an enormous error, and it is to be regretted that this has been publicly expressed. But as it has been done, nothing remains but to correct it.

Fittica is not able to state exactly the amount of arsenic contained in the phosphorus which he used in his experiments, because he found it very variable—from 0 to 2.64 per cent—according to the use of different oxidants, or to that of yellow or red phosphorus. The highest proportion of arsenic was found in red phosphorus, by oxidising it with nitric acid, while no arsenic could be discovered if the solution had been effected by barium peroxide and sulphuric acid. Fittica only roughly estimates that phosphorus had been transformed to the extent of from 8 to 10 per cent into arsenic, and a foundation for the above equation expressing the transformation, and the extraordinary formula PN_2O for the "synthetically produced" arsenic is quite wanting.

It has long been known that commercial phosphorus is often contaminated with arsenic. The arsenic is derived

from the sulphuric acid used for the decomposition of the calcium phosphate, and its percentage has been stated by Wittstock (*Pogg. Ann.*, xxxi., 126) at 0.76. At present it may be higher, because sulphuric acid is no longer prepared, as it was then, from sulphur, but almost without exception from arsenical pyrites. Hjelt (*Dingl. Pol. Journ.*, ccxxvi., 174) found in a chamber acid prepared from Rio Tinto pyrites 0.202 per cent of arsenic. If it be assumed that acid of this nature were used for the preparation of phosphoric acid, and that the total contents of arsenic went into the phosphorus obtained, the latter would contain 1.87 per cent of arsenic.

The determination of the amount of arsenic offers no difficulties whatever, but it, of course, requires the carrying out of proper analytical methods. The precipitation of arsenic by sulphuretted hydrogen may easily fail if the arsenic is present as arsenic acid, or if the solution contains other oxidising substances, like nitric acid, hydrogen peroxide, &c. But, as is well known, it easily succeeds on properly treating an acid solution of arsenious acid with sulphuretted hydrogen. On repeating the experiment described by Fittica, oxidising 2 grms. amorphous phosphorus with 12.9 grms. of ammonium nitrate, by carefully fusing them together, according to his prescription, it was found that it is not easy to properly moderate the reaction, but that, nevertheless, or perhaps more correctly in consequence of it, a small amount of phosphorus escapes the oxidation. The melt contains, in consequence, the arsenic present in the phosphorus, to a great extent in the form of arsenious acid, and its aqueous solution yields, therefore, with sulphuretted hydrogen, an immediate yellow precipitate of arsenic trisulphide. This is also the case if one operates in a manner which appears to me preferable, namely, by not adding the total quantity of amorphous phosphorus to the ammonium nitrate, but to fuse the latter in a large porcelain crucible at 170° C., and then to add the amorphous phosphorus in small portions, rapidly mixing them with a thermometer. Very soon evolution of gas takes place, and the temperature rises, but the reaction is quiet and free from danger, provided the source of heat is immediately removed when a temperature of from 180° to 190° has been reached. As soon as the phosphorus has disappeared, the temperature is allowed to fall, a second portion is added, and so on, until the operation is finished, which for 2 grms. of phosphorus requires about three hours. In proportion to the formation of phosphoric acid the melting-point of the mass falls, so that at the later stages the addition of phosphorus may be made at 140°, but the temperature is always again raised during the stirring to 170°, when it spontaneously rises to 180–190°. In this way the operation is almost quantitative, although small losses by spurting cannot quite be avoided. The reaction appears mainly to take place according to the equation,—



but as soon as the phosphoric acid begins to be in excess the reaction is influenced by it, a feeble odour of nitric acid being observable. The fumes which are formed in small amount are probably nothing else but volatilising ammonium nitrate.

The melt thus obtained was easily soluble in water, and the solution had a strongly acid reaction. It was made ammoniacal, and the arsenious acid oxidised into arsenic acid by hydrogen peroxide.

For comparison, three portions of 2 grms. each of the same sample of phosphorus, which had been previously washed with water and dried at 110°, were oxidised:—

(a). By heating with a mixture of 30 c.c. nitric acid of 1.185 sp. gr. and 10 c.c. of water.

(b). By passing chlorine into water wherein the phosphorus was suspended till the fluid was saturated, and subsequent removal of the excess of the gas by continued gentle heating.

(c). By heating with a solution of 10 grms. of purest sodium hydroxide, and occasional addition of hydrogen

peroxide, and subsequent acidulation of the solution with sulphuric acid.

The whole of these solutions were rendered ammoniacal, each evaporated to as small a volume as possible, and mixed with somewhat more than the calculated amount of an ammoniacal solution of ammonium magnesium chloride, of which 1 c.c. corresponded to 0.02 grm. of phosphorus. After the bulk of the precipitate had gone down more ammonia was added, and the mixture allowed to stand for forty hours. The washing of the precipitates was effected in the usual manner, with a mixture of one volume of ammonia to three volumes of water; no arsenic could be detected in the filtrate. The washed precipitates were dissolved in dilute sulphuric acid, and the solutions heated with repeated addition of sulphurous acid, and the excess of the latter expelled. They were then precipitated after dilution with sulphuretted hydrogen and allowed to stand overnight. The excess of sulphuretted hydrogen was mostly removed by gentle heating, but not entirely so; the arsenic trisulphide, which appeared to be of the same amount in all cases, was filtered off, dissolved on the filter in dilute warm ammonia, and the solution evaporated on the water-bath to dryness. The arsenic sulphide was then oxidised by nitric acid into arsenic acid, and this determined in the usual manner by precipitation with magnesia solution.

The amount of arsenic contained in the phosphorus was found to be as follows:—

	Per cent.
By oxidation with ammonium nitrate ..	1.910
“ “ nitric acid	1.925
“ “ chlorine	1.920
“ “ hydrogen peroxide ..	1.920

The percentage of arsenic was therefore found to be the same in all cases; rather too low by oxidation of the phosphorus with ammonium nitrate, because a small loss could not be avoided. It follows that there can be no question that the conversion of phosphorus into arsenic in the manner described—and one safely can say in any manner whatever—is out of the question, and that Fittica's statement is based upon an error.

It must be admitted that this matter, which I have discussed most unwillingly, involves a very serious consideration. It would appear as if in inorganic chemistry a dangerous tendency showed itself of late to enter into speculations without those careful investigations which have hitherto distinguished German chemists. Cases are multiplying which tend to show that a theory is first formed, and that then one seeks to find what one wishes to find, or that, in the words of the physiologist Czermak, one starts from “erroneously observed facts,” and thus falls into mistakes. The reason must be sought, to a great extent, in the fact that the art of analysis is being regrettably neglected. I intentionally say the “art,” for between analysing and analysing there is the same difference as between artists' and stonemasons' work. One cannot expect analytical aptitude from the physicist, whose field of investigation begins more and more to extend to inorganic chemistry as electrolysis develops, and he, within his field of investigation, is able to discover useful, even great facts. But physical chemistry is in no way synonymous with inorganic chemistry; for the latter, far from being a finished department of science, embraces problems in infinite number which must be solved upon an entirely different road than that indicated by the ion-theory. The really successful carrying out of inorganic chemical investigations is only possible to him who is not only a theoretical chemist, but also an accomplished analyst; not only a practical, mechanical workman, but a thinking and forming artist, who clearly sees the theories of the operations, to whom the knowledge of proportion is a part of himself, and who in all his doings is led by a sense of order and neatness, but especially by a desire for truth.—*Berichte*, xxxiii., No. 10, 1893.

Freiberg, Saxony, May 26th, 1900.

AN IMPROVED DOOR FOR LABORATORY
GAS FURNACE.

By B. A. BURRELL, F.I.C.

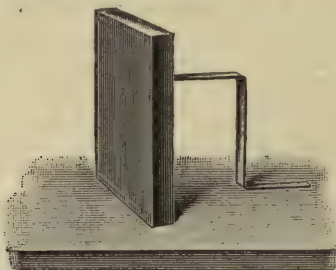
THE existing forms of doors for reverberatory gas furnaces are made of fire-clay or other refractory material, and have no outer casing; they are therefore easily broken, and not suited to withstand the rough usage they often receive from students.

Careless handling with the tongs soon causes the front projection to crumble away, and when this occurs they are awkward to move, and soon acquire a tendency to lean away from the furnace, leaving a gap between the furnace and the door, with consequent loss of heat. Further, all the existing forms of door, except Holloway's pattern, will not stand upright when removed from the furnace.

To overcome these objections I have devised the door shown in the accompanying cut:—

These doors have an outer casing of thin wrought-iron, except at the front, which is exposed to the interior of the furnace. At the front the outer casing only projects slightly round the four edges.

The bottom edge of the door is set at such an angle as to give the door a very slight backward tilt, but it is prevented from falling by the piece of bent hoop-iron inserted in a slot fixed on the back of the door; the door will thus stand upright when withdrawn from the furnace, and the hoop iron serves as a handle. (A piece of asbestos cloth should be used as a holder).



The two side edges of the casing are inclined at a slight angle from front to back, so that the front is slightly narrower than the back. Better fitting is thus obtained, and the lining of fireclay prevented from falling out.

The back of the iron casing is perforated with a number of small holes to permit of the more ready drying of the fire-clay mixture with which the door is lined. A suitable mixture for this purpose is composed of two-thirds raw fire-clay and one-third burnt fire-clay (by measure). A little sodium silicate added to the clay paste is advantageous.

The new door possesses the following advantages:—

1. It is practically indestructible, since the fireclay lining may be replaced at a merely nominal cost.
2. It can be adjusted so that it has no tendency to lean away from the furnace.
3. It stands upright when removed from the furnace.
4. It is cheaper than the furnace doors at present on the market.

An extended trial in this laboratory has resulted in the replacing of the plain fire-clay doors by the iron-bound doors, and the consequent abolition of a serious item of expense caused by frequent breakages.

The new doors may be obtained of Messrs. John J. Griffin and Sons, who supply them in sizes to fit their Holloway Gas Furnace or other sizes as required.

Metallurgical Laboratory,
Leeds Technical School.

SYNTHESIS OF SOME ORGANIC COMPOUNDS
BY MEANS OF FERRIC CHLORIDE.

By N. MEISSEL.

THE condensation of *m*-xylene with chloride of acetyl in the presence of ferric chloride commences readily in the cold; it is finished by heating for twenty minutes on the water-bath; the product is then washed with water, and collected by the help of steam. In this manner we obtain dimethylacetophenone, $\text{CH}_3\text{CO}\cdot\text{C}_6\text{H}_3(\text{CH}_3)_2$, in the form of a liquid having an agreeable smell and a density of 1.0121 at 15°; its boiling-point is 227–228°. A small quantity of *o*,*p*-xylylic acids is also formed. The return is 30 per cent, but if we make use of a sulphocarbonic solution we can obtain as much as 75 per cent. In the same manner the author has prepared dimethylbenzophenone boiling at 362° (a return of 70 per cent), cymylmethylketone, $\text{CH}_3\text{C}_6\text{H}_3(\text{COCH}_3)\cdot\text{CH}(\text{CH}_3)_2$, a liquid of 0.9715 density at 15°, boiling at 240–242°, and giving a red colouration with ferric chloride in alcoholic solution. The tertiary chloride of butyl does not condense with *p*-xylene in the presence of ferric chloride; on the other hand, chloride of acetyl reacts on *p*-butyltoluene (tertiary) readily in the cold, giving rise principally to butylmethylacetophenone (72 per cent), an oily liquid with an agreeable odour, insoluble in water; $d = 0.9541$ at 15°; the alcoholic solution is coloured red by ferric chloride. The condensation of tetrachloride of carbon with benzene gives, uniquely, chlorised triphenylmethane, $\text{Cl}\cdot\text{C}(\text{C}_6\text{H}_5)_3$, which is transformed by water into triphenylcarbinol; with chloroform and benzene we obtain a mixture of carbinol and triphenylmethane (we use 1 part of chloroform, 1 part of ferric chloride, and 6 parts of benzene, and heat on the water-bath). The condensation of the chlorocarbonate of iso-amyl with phenol gave *p*-iso-amylphenol, fusible at 93–94°; in the same manner, with the chlorocarbonate of ethyl, we obtain *p*-ethylphenol.—*Berichte*, xxxii., p. 2419.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING MAY 31ST, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of May shows that the drought still continues. The actual fall was 1.33

inches; the average fall is 1·83 inches; this leaves a deficit of 0·50 inch for the month, and reduces the previous excess for the year to 0·34 inch, or 3·8 per cent on the thirty years' average.

Our bacteriological examinations of 557 samples have given the results recorded in the following table; we have also examined 36 other samples, from special stand-pipes, &c., making 593 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	104
New River, filtered (mean of 131 samples) ..	6
Thames, unfiltered (mean of 27 samples) ..	932
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 304 samples)	19
Ditto ditto highest	372
Ditto ditto lowest	6
River Lea, unfiltered (mean of 27 samples) ..	283
River Lea, from the East London Company's clear-water wells (mean of 41 samples) ..	6

The chief characteristic of the London waters during the month of May is the comparative microbic purity of the unfiltered waters of the New River, Lea, and Thames. During the month all the 557 samples examined from the clear-water wells showed that the filtration was being properly conducted, and was highly efficient as regards the elimination of microbes, with the exception that one of the Companies' wells on one occasion showed a higher number than 300 microbes. This arose from a purely local cause in one of the filters. It was at once remedied, and the action of the filter returned to its normal state of efficiency.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 7th, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

(Concluded from p. 255).

82. "The Ultra-violet Absorption Spectra of some Closed Chain Carbon Compounds. II. Dimethylpyrazine, Hexamethylene, and Tetrahydrobenzene." By W. N. HARTLEY, F.R.S., and JAS. J. DOBBIE, D.Sc., M.A.

It was shown by the authors that dimethylpyrazine, a substance representing a group not hitherto examined spectroscopically, possesses a banded spectrum, the absorption band being both wider and more persistent than that of pyridine. This result was anticipated from the analogy of the constitution of this substance with that of benzene and pyridine. It affords further evidence of the intimate connection between the phenomenon of selective absorption and the benzenoid structure.

The result is further interesting in connection with the question of the constitution of cyanuric acid (*Trans.*, 1882, xli., 48). While pyridine contains the group C:N once in the benzene structure, dimethylpyrazine contains it twice, and the formula originally proposed for cyanuric acid contains it three times. Accordingly, if this formula were correct for cyanuric acid, we should expect that it would exhibit a powerful absorption band more intense than that of pyrazine. It has, however, been recently shown (Hartley, *Proc.*, 1899, xv., 46) that cyanuric acid has no absorption band.

Specimens of pure hexamethylene and tetrahydrobenzene, prepared by Professor Sydney Young and Miss Fortey, and kindly lent by them, were found to be much more highly diazinic than benzene, and showed no trace

of selective absorption. This result confirms the conclusion, previously drawn from the examination of such substances as hexachlorobenzene and piperidine (*Phil. Trans.*, 1885, Part II.), that with reduction of the benzene ring the substances are no longer characterised by an absorption band, but by a continuous spectrum indicating a less compact form of linking within the nucleus of the carbon atoms or of the carbon and nitrogen.

83. "A Study of the Absorption Spectra of *o*-Oxycarbanil and its Alkyl Derivatives in relation to Tautomerism." By W. N. HARTLEY, F.R.S., JAS. J. DOBBIE, D.Sc., M.A., and PHOTIOS G. PALIATSEAS.

Two ethyl derivatives of *o*-oxycarbanil, $\text{C}_7\text{H}_5\text{NO}_2$, are known. One of these is prepared directly from *o*-oxycarbanil by boiling it with equivalent quantities of ethyl iodide and alcoholic potash. This ether is considered to have the lactam constitution, because when heated with hydrochloric acid it takes up water and decomposes into carbon dioxide and the hydrochloride of ethyl-*o*-amido-phenol. The other ether, which is obtained by the interaction of *o*-amido phenol and ethyl imido-carbonate, yields oxycarbanil on treatment with strong hydrochloric acid, and is therefore a lactime. The chemical evidence leaves it undecided whether *o*-oxycarbanil itself possesses the lactam or the lactime structure. On photographing the absorption spectra of the three compounds it was found that the spectra of *o*-oxycarbanil are almost identical with those of the lactam ether. The amount of general absorption is practically the same in both cases, and the absorption band, which is well marked and persistent, occupies the same position in the spectra of both substances. The spectra of the lactime ether show a smaller amount of general absorption and the absorption band is much less persistent. From the similarity between the spectra of *o*-oxycarbanil and the lactam ether, it is inferred that the parent substance in this case, as in the cases of isatin and carbostyryl (*Trans.*, 1899, lxxv., 640), possesses in solution the ketonic structure, or—if the solution be a mixture of tautomeric modifications—that the ketonic modification predominates almost to the exclusion of the enolic.

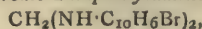
84. "Action of Formaldehyde on Amines of the Naphthalene Series." II. By G. T. MORGAN, D.Sc.

By the action of formaldehyde on ethyl- β -naphthylamine, 2 : 2-diethyldiamino-1 : 1-dinaphthylmethane, melting at 197–198°, is obtained when the reaction is carried out in cold glacial acetic acid, but when the condensation is effected in hot alcoholic solutions in the presence of hydrogen chloride, it is accompanied by a compound, $\text{C}_{23}\text{H}_{19}\text{NO}$ (m. p. 157–158°).

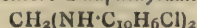
2 : 2-Dibenzoyldiethyl-1 : 1-dinaphthylmethane, produced from the preceding diamine by the Schotten-Baumann reaction, melts at 196°.

1 : 1-Tetramethyldiaminodinaphthylmethane, prepared from dimethyl- α -naphthylamine, melts at 177°; unlike its benzenoid analogue, tetramethyldiaminodiphenylmethane, it does not yield a colour base on treatment with lead peroxide.

Further investigation of the methylene bases derived from 1-bromo-2-naphthylamine and 1-chloro-2-naphthylamine has shown that these substances cannot be formulated on the type $\text{CH}_2\text{:NR}$, as indicated in the preliminary note (*Proc.*, 1899, xv., 10), but have the constitution indicated by the formula $\text{CH}_2(\text{NHR})_2$. They do not combine additively with anhydrous hydrogen cyanide, and when treated with phloroglucinol (Tollens's reagent, *Ber.*, 1899, xxxii., 2841), they are quantitatively decomposed, yielding 2 mols. of the parent base and 1 equivalent of methylene-phloroglucinol ($\text{C}_7\text{H}_6\text{O}_3$). It follows from these results that the bromo- and chloro-derivatives must be regarded as methylenedi-1-bromo-2-naphthylamine,—



and methylenedi-1-chloro-2-naphthylamine,—



respectively.

85. "The Bromination of Benzeneazophenol." II. By J. T. HEWITT and W. G. ASTON.

When benzeneazophenol is brominated in a glacial acetic acid solution containing an excess of fused sodium acetate, an almost theoretical quantity of benzeneazoorthodibromophenol is obtained. If, however, the sodium acetate be omitted, a tribromo-derivative is formed, having a constitution hitherto unknown. The same product is obtained by bromination in aqueous suspension. This substance has now been proved to be *parabromobenzene-azoorthodibromophenol*. The proof has been furnished by brominating parabromobenzeneazophenol in presence of sodium acetate, and benzeneazoorthodibromophenol in presence of sulphuric acid. The same substance was obtained in both cases, and is identical with that obtained by the direct action of bromine on benzeneazophenol as described above. The corrected melting-point of the substance is 148° , and it has been further characterised by conversion into derivatives.

Acetyl ester, m. p. 167° ; *benzoyl ester*, m. p. 129° ; *ethyl ether*, m. p. 125° .

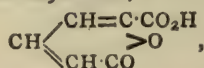
The isomeric *tribromobenzeneazophenol*, which was prepared from symmetrical tribromaniline for purposes of comparison, and contains the bromine entirely in the benzene nucleus, melts at 168.5° , its *acetyl* derivative at 105° , and its *benzoyl* derivative at 132° .

86. "Condensation of Ethyl Crotonate with Ethyl Oxalate." By ARTHUR LAPWORTH.

A consideration of the points alluded to in a recent note (*Proc.*, 1900, xvi., 108), made it appear probable that ethyl crotonate and allied compounds would react in presence of sodium ethoxide with esters such as ethyl oxalate, and that substitution would occur, not in the α -position as usual, but in the γ -position, corresponding with the *meta*-position in benzoic acid, and to the position occupied by the hydrogen atoms in the methyl group of *o*- and *p*-nitrotoluene. This has been found to be the case.

Ethyl γ -oxalocrotonate, $\text{EtO}_2\text{C}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$, is easily prepared from ethyl crotonate and ethyl oxalate by the use of alcohol-free sodium ethoxide. It acts as a fairly strong acid, expelling carbon dioxide from carbonates, and yielding strongly coloured metallic derivatives. Its alcoholic solution is coloured brownish-black by ferric chloride, so that it exists, to some extent at least, in its "enolic" form. It forms nearly colourless crystals melting at $78-80^{\circ}$.

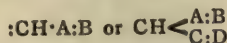
When ethyl γ -oxalocrotonate is hydrolysed by boiling with alkalis it does not give oxalic acid; with hydrochloric acid, *α -pyrone- α' -carboxylic acid*,—



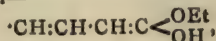
is obtained. This separates from hydrochloric acid in colourless crystals melting at $227-228^{\circ}$.

The formation of ethyl γ -oxalocrotonate in the above manner recalls the observations of Henrich on ethyl glutaconate (*Ber.*, 1898, xxxi., 2103), but in the present case the $-\text{CH}_2-$ group is not united to two unsaturated groups.

There are many facts bearing on "the negative nature of unsaturated groupings" which seem to point to the insufficiency of the view that the hydrogen atom in the grouping—



is of itself immediately replaceable, and it appears more likely that the position of attack is usually at a double linkage (compare Henrich, *Ber.*, 1900, xxxiii., 1437). In the above case, as in many similar ones, it appears not improbable that an intermediate compound derived from a tautomeric form—



is produced, and that subsequently, either by addition or

isomeric change or by both, the γ -carbon atom becomes united with the substituting group (*Trans.*, 1898, lxxiii., 446).

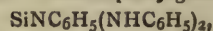
The author proposes to extend the above observations, and to examine the capability of other $\alpha\beta$ -unsaturated esters of taking part in this and similar condensations.

87. "Researches in Silicon Compounds. VI. On Silicodiphenyldiimide and Silicotriphenylguanidine." By J. EMERSON KEYNOLDS, Sc.D., M.D., F.R.S.

The author has already described (*Trans.*, 1889, lv., 474) the well defined crystalline silicophenylamide, $\text{Si}(\text{NHC}_6\text{H}_5)_4$, the first of a new class of compounds in which silicon is exclusively united to nitrogen. It was there stated that when this compound was heated in a vacuum to its melting-point (137°) some aniline was given off and a mixture of silicon compounds formed, the constituents of which would be described later. The nature of these products was stated shortly afterwards to the British Association in 1893, but no details were then given. These are now described, before an account of more recent investigations is presented to the Society.

The primary interest attached to the examination of the changes effected by heating silicophenylamide is due to the probable production of silicon analogues of cyanogen compounds.

The study of the action of heat revealed the formation of the *diimide*, $\text{Si}(\text{NPh})_2$, which exists in two modifications, one insoluble in benzene and the other soluble, but precipitated by ligroin in droplets which slowly change to the insoluble form. *Silicotriphenylguanidine*,—



was isolated from the earlier products of the action of heat in small, short rhombic prisms, soluble in benzene. Like all other organic silicon compounds of this kind, it is decomposed by acids, as well as by water and alcohol.

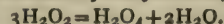
The continued action of heat on the diimide gave rise to a compound represented by the formula $\text{Si}_2(\text{NC}_6\text{H}_5)_3$; this withstood a high temperature without charring, and when heated in dry ammonia left a residue which approximated in composition to $\text{Si}_2(\text{NH})_2\text{NC}_6\text{H}_5$, but the decomposition could not be carried beyond this point without the separation of carbon.

88. "Note on Bach's Hydrogen Tetroxide." By HENRY E. ARMSTRONG.

It is contended by A. Bach (*Ber.*, 1900, xxxiii., 1506) that the liquid obtained on mixing a solution of hydrogen peroxide with sulphuric acid probably contains hydrogen tetroxide. He bases this conclusion on the observation that when the amount of permanganate which the solution decolorises is contrasted with the amount of oxygen which is evolved, the latter is largely in excess of that which would be obtained if only hydrogen peroxide were present. Bach has obviously failed to take into account the existence of persulphuric acid in such a solution.

In all his experiments—both in those in which palladium hydrogen was oxidised and in those with peroxides—a large excess of normal sulphuric acid was added; the solution was then titrated with permanganate, and the oxygen which was given off was collected and measured. It is noteworthy that the liquid was shaken during several minutes (5–8) after the titration was completed in order to expel the gas. It is open to question whether, in these cases, some persulphuric acid was not formed (Lowry and West, p. 126) by peroxidation of the sulphuric acid, and whether the extra oxygen obtained by Bach was not derived from this.

Bach regards the fact that other dehydrating agents besides sulphuric acid—for example, hydrogen chloride—produce effects, when mixed with hydrogen peroxide, similar to those obtained on using Caro's reagent, as evidence in favour of the view that hydrogen peroxide is converted into tetroxide by dehydration,—



It may be pointed out, however, that the effects produced

by Caro's reagent are merely such as it might be anticipated would be exercised by hydrogen peroxide acting in presence of a powerful dehydrating and hydrolysing agent, and it is the use of hydrogen peroxide under such conditions that characterises the novelty in procedure. It is not necessary to assume the existence of any novel specific agent in order to explain them. Caro's original observations stand on a different plane, as they served to establish a difference between the perdisulphates and salts of another acid, and for the first time made it possible to differentiate the acid products of the electrolysis of sulphuric acid.

PHYSICAL SOCIETY.

Ordinary Meeting, June 22nd, 1900.

Mr. T. H. BLAKESLEY, Vice-President, in the Chair.

A PAPER entitled "*Notes on Gas Thermometry*," by Dr. P. CHAPPUIS, was read by Dr. HARKER.

The author, having been led to recognise that hydrogen could not be used as a thermometric substance at high temperatures, on account of its action on the walls of the glass reservoirs, has had recourse to a constant volume nitrogen thermometer with an initial pressure slightly under 800 m.m. The value of the coefficient of expansion of nitrogen at constant volume is variable, diminishing up to 80° C. and then increasing slightly. In fact, nitrogen at 100° C. behaves like hydrogen at the ordinary temperatures, its compressibility being less than that required by Boyle's law. A table of corrections was therefore prepared. The readings of the constant volume nitrogen thermometer are too low, but the corrections are small, amounting to about 0.04° C. at the temperature of boiling sulphur. The mean result of the author's experiments for the boiling-point of sulphur is 445.2° under a pressure of 760 m.m. Callendar and Griffiths' result, obtained with a constant pressure air thermometer, is 444.53°. The difference is attributed to the joint action of several causes:—(1) The corrections for a constant pressure thermometer are about double those of a constant volume instrument; this correction applied to Callendar and Griffiths' result would raise it about 0.1°. (2) Callendar and Griffiths have used a value for the gas constant which is larger than that obtained by more recent experiments; adopting the latter value the boiling-point would be raised to 445°. (3) The divergence may be due to the expansion of the reservoir. The most accurate way of determining this is by the interference method of Fizeau. This method is used with small pieces of the material, and the author has employed it to determine the coefficient of expansion between 0° and 100°. Extrapolation to 450° might cause errors. The linear expansion has recently been determined by Bedford between 0° and 840°, by a comparator method. The homogeneity of porcelain is doubtful, especially when glazed, and the great differences occurring between the expansions obtained from the above methods is attributed to the change in form of the tube in Bedford's experiments, brought about by unequal thickness and want of homogeneity, and consequent unequal expansion. The author, therefore, adheres to his value of the boiling-point obtained from the expansion by the Fizeau method, whilst recognising the uncertainty attaching to the application of the coefficient of expansion of the reservoir over an interval four times as great as that over which it was determined.

A paper on "*A Comparison of Impure Platinum Thermometers*," by Mr. H. M. TORV, was read by Prof. CALLENDAR.

The object of this paper is to investigate the probable order of accuracy attainable in the determination of high temperatures by the use of ordinary commercial specimens of platinum wire. Five wires were compared from 400° to 1000° C. The fundamental coefficients of the

wires varied within 40 per cent of the maximum value, but the temperatures observed by them—when calculated on the platinum scale by means of the ordinary simple formula—did not differ by more than 9° at 1000° C. Each wire was directly compared with a pure standard wire, the two being wound side by side in the same tube. Curves have been drawn with the platinum temperatures of the standard wire as abscissae, and the differences between the temperatures indicated by the two wires compared as ordinates. These curves are all straight lines, within the limits of observation, and hence the determination of two constants is sufficient to enable us to compare an impure platinum thermometer with the standard, and therefore with the scale of the gas thermometer. The two constants can at once be obtained from observations at the boiling-point of sulphur and the freezing-point of silver, and thus a practical thermometric scale can be established, which between 0° and 1000° never differs by more than two or three degrees from the gas scale.

Prof. CALLENDAR said he was unable to agree with the correction to his observations suggested by M. P. Chappuis. He considered that the uncertainty in the coefficient of expansion of the gas was due to uncertain changes in the volume of the bulb, and to uncertainty in the coefficient of expansion of mercury. The fundamental coefficient of mercury was 0.00018153 according to Regnault, 0.00018216 according to the later reduction of Broch, and 0.00018256 according to experiments by Chappuis with a hard glass bulb. It made a difference of no less than 4 per cent in the fundamental coefficient of expansion of the glass, according as the original results of Regnault, or the value found by Chappuis assuming the linear expansion of the glass, were adopted. The importance of the changes in the volume of the bulb had been fully pointed out, and a method of taking approximate account of these changes had been explained in the paper on the boiling-point of sulphur in 1890. Unfortunately the glass employed was rather soft, and the changes of volume which occurred were too great to permit of the most accurate determination of the coefficient. The boiling-point when corrected for the smaller expansion of the bulb came out lower than 444.53. With regard to porcelain, Prof. Callendar did not consider it a good material, on account of the glaze. He did not think that the average coefficient of a tube or bulb over a large range of temperature could be inferred from a small and possibly asymmetric specimen. The results might be less inconsistent in the case of homogeneous and well-annealed metallic bulbs. The correction for the expansion of the bulb was, he believed, given by the expression $dt = (c + b\theta) \cdot t(t - 100)$. He did not agree with M. P. Chappuis that the correction was independent of c , although the value of b was certainly most important at high temperatures. He also wished to take exception to the method adopted by Chappuis of calculating the correction of the nitrogen thermometer. According to Joule and Thomson the correction should be greater; according to other authorities it might be less. He hoped to discuss this in a future communication to the Society.

Mr. GLAZEBROOK said that, although he placed confidence in Chappuis' formula for a definite piece of porcelain between certain temperatures, he thought further and careful work was necessary before fixing on a formula for ordinary use.

Prof. CARHART said he would like to see a comparison made between the results of experiments with gas thermometers and those with platinum and platinum-rhodium couples.

Mr. ROSE-INNES expressed his interest in the behaviour of nitrogen about 100° C., as mentioned in M. Chappuis' paper.

Dr. LEHFELDT said the peculiarities of the nitrogen scale between 70° and 80° might be explained by the reversal of the properties of nitrogen between 0° and 100°.

A paper on "*The Law of Cailletet and Mathias, and the Critical Density*," was read by Prof. S. YOUNG.

The law of Cailletet and Mathias is very nearly, though in most cases not absolutely, true. It appears to be only strictly true when the ratio of the actual to the theoretical density at the critical point has the normal value 3.77. The curvature of the "diameter" is generally smaller the nearer this ratio approaches its normal value. The curvature is in nearly every case in opposite directions, according as this ratio is greater or less than 3.77. The curvature is generally so slight that the critical density may be calculated from the mean densities of liquid and saturated vapour at temperatures from about the boiling-point to within a few degrees of the critical point, with an error generally not exceeding 0.1 per cent. If, however, the critical density is calculated from the mean densities at low temperatures, the error may be considerable; in the case of normal decane it is between 5 and 6 per cent. The law does not, as a rule, hold good at all for substances the molecules of which differ in complexity in the gaseous and liquid states.

Mr. ROSE-INNES said that in his paper the author had used the generalisations of van der Waals, although the author himself had shown that they were not strictly true.

Prof. YOUNG said that the generalisations held in some cases, although they did not in others. In all cases they were approximately true, and it was therefore advisable to use them, and study the results as far as possible.

The Society then adjourned until next October.

NOTICES OF BOOKS.

Compulsory Licenses under the Patents Acts. By J. W. GORDON. Stevens and Sons, Lim., Chancery Lane.

MR. GORDON has written a treatise on Clause 22 of the Patent Law of 1883, which should be of value to all classes of the community; to lawyers, as giving a clear account of the manner in which the Board of Trade is administering the novel powers conferred on it seventeen years ago; to patentees, as showing how the privileges which they claimed, and in some cases misused, are modified or abolished; and to the public at large, and especially manufacturers of patented goods, as showing the steps taken by the legislature to restore to them their ancient rights under the common law which they had, largely by their own supineness, allowed to be wrested from them.

Mr. Gordon, in explaining the privileges and obligations conferred on patentees by their grants, takes us back three hundred years, and shows us that, in the conditions then prevailing, the grant in the majority of cases served two purposes; the first was to enable the patentee to work his patent, the second was to secure to him a sufficient reward according to the merit of his invention. In early days the former was the all-important purpose, while so little was the latter considered that it was stipulated that should the working of the patent be to the detriment of the commonwealth, the grant would be cancelled. Of late years the former reason has, by virtue of changing circumstances, become obsolete, while patent owners have, as is natural, made full use of the latter.

When all the trades in the kingdom were governed by Chartered Guilds, and it was impossible for any person to practise his trade in any place where he was not a freeman, it was a necessary act on the part of the Crown for the general good of the community to confer "personal charters" or patents on inventors to enable them to work their inventions; but, lest they should use their privileged position to stifle an existing industry for their own personal gain, a drastic penalty clause was inserted, and, to make the purpose of the grant still clearer, it was expressly stated the reward, if any, gained by the inventor, was

because he had introduced a new industry into the kingdom.

Since the decay of the Guilds, inventors and their backers have in many instances used their powers solely for their own profit, irrespective of the public good, whilst the penalty clause appears to have been forgotten.

In 1883 the Government passed an Act authorising the Board of Trade to compel a patentee to grant licenses to others to work his patent on terms to be decided by them, for either of three reasons duly set forth in Clause 22.

For various reasons this clause was not called into use for fifteen years; but in the last two years several applications for compulsory licenses have been made to the Board with varying success, and in the second part of his book Mr. Gordon discusses these cases, showing how various legal points were raised and disposed of, and why certain cases broke down, whilst others, which were superficially similar, succeeded.

This part of the book should be of assistance to lawyers, since it can hardly be doubted that the forms and procedures now being hammered out will serve as precedents to be followed in future cases.

The book is well written in language to be easily understood by the lay reader, though in many cases the punctuation is unorthodox; this is possibly due to the well-known antipathy between lawyers and all stops but periods. This slight blemish can be easily remedied in the next edition.

Outlines of Physical Chemistry. By A. REYCHLER. Translated by Dr. JOHN McCRAE. London and New York: Whittaker and Co.

THE ground covered by this work is very extensive, and, as it is but a small volume, it is aptly labelled "Outlines."

Although there is no direct statement to that effect, the work appears to be based on a course of lectures delivered by Prof. Reychler at the University of Brussels, and would thus be of great value to students at that Institution; still the wisdom of adding it to the mass of technical literature already published in England is not obvious.

Prof. Reychler has treated his subject in four parts, with subdivisions.

In the first part he begins with stating the laws of chemical combination, leading to a discussion on gases and vapours under pressure, and by an easy transition to the methods of determining atomic weights, and concludes with a comparison of Mendeléeff's and L. Meyer's classification of the elements.

The second part treats of the transformation of matter through the solid, liquid, and gaseous states, with an examination of the phenomena of polarisation.

Thermo- and electro-chemistry are considered in the third part, and chemical mechanics in the fourth.

The author's views are in many cases not to be divined, for he sets forth opposing theories with the objections to each with such impartiality that one can only conclude that both are equally correct in his opinion.

A feature that might be more widely adopted is a complete index of author's names.

The illustrations are clear, and show all that is necessary without useless details.

The Tutorial Dynamics. By WILLIAM BRIGGS, M.A., &c., and G. H. BRYAN, Sc.D., F.R.S. London: Published by W. B. CLIVE.

THIS is one of a series of books written and published for that large and increasing class of students who study at home and correspond by post with their tutors. The authors have treated their subject in a very simple manner, the use of the calculus being altogether ignored, since they have found by experience that it is a dangerous weapon to put into the hands of men who are not thoroughly grounded in the elements of mechanics.

The volume covers the ground usually treated in such books, and does so in a satisfactory manner; it is as well, however, to point out that in Chapter XIV., on Motion down Inclined Planes, the inclination of "1 in n" is defined as the ratio of height to length, whereas engineers invariably use the ratio of height to base. The examples are numerous and well chosen. The addition of an index would be an improvement.

CORRESPONDENCE.

DISTILLATION WITHOUT BUMPING.

To the Editor of the Chemical News.

SIR,—If the Rev. G. F. M. Fielding will kindly refer to Perkin and Kipping's "Organic Chemistry," vol. 1, p. 16, he will find the following statement:—

"A few scraps of unglazed porcelain . . . prevent bumping."

Also, Gattermann, "Organic Chemistry," p. 30:—

" . . . pieces of porcelain, powdered talc, . . . pieces of pumice bound with Pt wire " prevent bumping.

Also, Streasfeld's "Organic Chemistry," p. 10:—

"Two or three pieces of broken pipe-clay are added in order to prevent bumping."

Although pieces of broken tobacco-pipe are not mentioned, unglazed porcelain is very similar, and in my experience has always yielded good results.—I am, &c.,

CHEMICO.

DISTILLATION WITHOUT BUMPING.

To the Editor of the Chemical News.

SIR,—Mr. Fielding's suggestion, that in order to prevent bumping during distillation, small fragments of common tobacco pipes are very efficient, is one which in principle is pretty generally known. Tobacco piping itself may not be used, but unglazed earthenware (such as is used for drying chemicals) or other porous materials are extensively employed.

As Mr. Fielding (re his reply to "A Ghost of 200 Years") has only come across one suggestion, I may refer him to Gattermann's excellent little book on "Practical Methods of Organic Chemistry" (English translation, The Macmillan Co., 1896), where he will find some 18 pages devoted to distillation, and on page 30 the following substances recommended:—"Splinters of wood the size of a match, capillary tubes, bits of glass, pieces of porcelain, powdered talc, scraps of platinum foil or wire, small pieces of pumice stone, bound with platinum wire, also act satisfactorily."

As such a book as Gattermann is in most laboratories, Mr. Fielding need not be surprised when he gets such an answer as that from "A Ghost of 200 Years." His letters, however, furnish a reason why such letters should be published, letters which I thought were quite unnecessary.—I am, &c.,

W. R.

DISTILLATION WITHOUT BUMPING.

To the Editor of the Chemical News.

SIR,—If Mr. Fielding will refer to "Allen's Commercial Organic Analysis," vol. iv., p. 150, he will find the following:—" . . . and a few fragments of pumice or tobacco-pipe added to prevent bumping."—I am, &c.,

W. A. CATES.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 22, May 28, 1900.

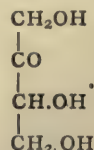
Formation of Nitric Acid in Combustions.—M. Berthelot.—The author continues his researches on the formation of nitric acid during combustions. He considers the case of the burning of sulphur in oxygen containing 8 per cent of nitrogen, under different pressures, and also in atmospheric air. The next series of experiments are performed on metals, to find what proportion of nitrogen becomes combined during the combustion of metals. The two metals used are iron and zinc.

Preparation, Properties, and Analysis of Thionyl Fluoride.—H. Moissan and P. Lebeau.—During the preliminary experiments, the authors found that when fluorine acts on sulphur in a glass vessel a mixture of fluorides and oxyfluorides of sulphur are formed, amongst which fluoride of thionyl can be recognised, SOF_2 . This substance, after separation from the other fluorides, appears as a colourless gas, fuming in damp air, and with a disagreeable odour. Its boiling-point is about -32° , and density varies between 2.88 and 3.04, the theoretical number being 2.97. It is soluble in arsenic chloride, ether, essence of terebenthine, and benzene. The action of heat on this substance in the presence of glass allows of the determination of its composition by volume. Four volumes of SOF_2 giving four volumes of SO_2 and two volumes of SiF_4 .

A Peroxide of Lithium.—M. de Forcrand.—The combustion of lithium in an atmosphere of oxygen gives mere traces of the peroxide; this body appearing to dissociate into the protoxide and oxygen. The author finds that, using the wet method of preparation, by allowing peroxide of hydrogen to act on a solution of lithia, a peroxide is formed. Two separate experiments were tried; the crystals separating out in the two cases having formulæ $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 + 3.07\text{H}_2\text{O}$ and $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 + 2.77\text{H}_2\text{O}$.

The Unknown Earths contained in Crude Samaria.—Eug. Demarçay.—The author previously announced that he had obtained from crude samaria a new element characterised by several spectrum lines, and having an atomic weight higher than that of samarium and lower than that of gadolinium. This substance he now obtains in a greater state of purity. The earth is white, slightly tinged with rose-pink; the salts being of a pale rose, and showing the following absorption bands in the nitric solution:—590, 570, 535, 525, 465, 395.5, 385.5, 380.5; none of these bands being strong. The characteristic spark spectrum lines are also given. The atomic weight of this element is about 151.

Hydrogenation of Erythrulose and Preparation of a New Erythrite, Dextro-erythrite.—Gabriel Bertrand.—The author has already shown that erythrite is rapidly oxidised by the bacteria of sorbose, and from it is obtained a syrup composed almost entirely of erythrulose. This new sugar contains four atoms of carbon, and has the formula—



By the fixation of one molecule of hydrogen, two stereoisomeric erythrites are formed: one inactive and identical with natural erythrite, the other optically active. This double transformation is effected by means of sodium amalgam.

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THE CHEMICAL NEWS, JANUARY 11, 1901.

THE
CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXXII.—1900.

LONDON:

PUBLISHED AT THE OFFICE, 6 & 7, CREED LANE, LUDGATE HILL, E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCC.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
6 & 7, CREED LANE, LUDGATE HILL,
E.C.

THE CHEMICAL NEWS.

VOLUME LXXXII.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2119.—JULY 6, 1900.

ON THE VISCOSITY OF GASES AS AFFECTED BY TEMPERATURE.*

By Lord RAYLEIGH, F.R.S.

A FORMER paper (*Roy. Soc. Proc.*, 1900, lvi., p. 68; *CHEM. NEWS*, lxxxi., p. 85) describes the apparatus by which I examined the influence of temperature upon the viscosity of argon and other gases. I have recently had the opportunity of testing, in the same way, an interesting sample of gas prepared by Professor Dewar, being the residue, uncondensed by liquid hydrogen, from a large quantity collected at the Bath springs. As was to be expected (*Roy. Soc. Proc.*, 1896, lix., p. 207; 1896, lx., p. 56), it consists mainly of helium, as is evidenced by its spectrum when rendered luminous in a vacuum tube. A line, not visible from another helium tube, approximately in the position of D_2 (Neon) is also apparent.†

The result of the comparison of viscosities at about 100° C., and at the temperature of the room, was to show that the temperature effect was the same as for hydrogen.

In the former paper the results were reduced so as to show to what power (n) of the absolute temperature the viscosity was proportional.

	n .	c .
Air.. ..	0.754	111.3
Oxygen.. ..	0.782	128.2
Hydrogen }	0.681	72.2
Helium }		
Argon	0.815	150.2

Since practically only two points on the temperature curve were examined, the numbers obtained were of course of no avail to determine whether or no any power of the temperature was adequate to represent the complete curve. The question of the dependence of viscosity upon temperature has been studied by Sutherland (*Phil. Mag.*, 1893, xxxvi., p. 507), on the basis of a theoretical argument which, if not absolutely vigorous, is still entitled to considerable weight. He deduces from a special form of the kinetic theory as the function of temperature to which the viscosity is proportional—

$$\frac{\eta}{1 + c/\theta} \dots \dots \dots (1).$$

* A Paper read before the Royal Society, June 21, 1900.

† I speak doubtfully, because to my eye the interval from D_1 to D_2 (helium) appeared about equal to that between D_2 and the line in question, whereas, according to the measurements of Ramsay and Travers (*Roy. Soc. Proc.*, 1898, lxi., p. 438), the wave-lengths are—

D_1	5895.0
D_2	5890.0
D_3	5875.9
D_4	5849.6

so that the above-mentioned intervals would be as 19.1:26.3. I may record that the refractivity of the gas now under discussion is 0.132 relatively to air.

c being some constant proper to the particular gas. The simple law $\eta \propto \theta^{\frac{1}{2}}$, appropriate to "hard spheres," here appears as the limiting form when θ is very great. In this case, the collisions are sensibly uninfluenced by the molecular forces, which may act at distances exceeding that of impact. When, on the other hand, the temperature and the molecular velocities are lower, the mutual attraction of molecules which pass near one another increases the number of collisions, much as if the diameter of the spheres was increased. Sutherland finds a very good agreement between this formula (1) and the observations of Holman and others upon various gases.

If the law be assumed, my observations suffice to determine the values of c . They are shown in the table, and they agree well with the numbers for air and oxygen calculated by Sutherland from observations of Obermayer.

THE SENSITIVENESS OF SILVER AND OF SOME OTHER METALS TO LIGHT.*

By Major-General J. WATERHOUSE, I.S.C.,
(late Assistant Surveyor-General of India).

DURING some recent investigations on the Daguerreotype process, the question presented itself as to which of the elements forming the sensitive surface of the plate—the silver or the halogens—the sensitiveness was due? Now, although the fact that nearly all compounds of silver, especially the haloids, are more or less sensitive to, and decomposed by, the action of light, has long been known, the sensitiveness of metallic silver itself to light, though observed in 1842 by Moser, has never been generally recognised either by chemists or by photographers.

Moser's Experiment.—Before describing my own experiments, it may be as well to give a description of Moser's experiment taken from the original paper in *Poggendorff's Annalen*, 1842, vol. lvi., p. 210.

"A perfectly new silver plate was thoroughly cleaned and polished. A black tablet with various excised characters was fixed above it, without touching it, and the whole placed in the sun for two hours or more and directed towards it. After the plate, which naturally did not show the least change, was cooled, it was held over mercury, heated as usual to about 60° R. (167° F.). To my great delight a distinct image of the screen was produced in which those parts where the sunlight (which during the course of the experiments was always weak and changeable) had acted had attracted a quantity of mercury. This interesting experiment was repeated

* A Paper read before the Royal Society, May 31, 1900.

several times with the same result. Sometimes the plates after having been placed in the mercurial vapours were exposed to those of iodine and then placed in the sun, by which the images usually improved."

"If we compare this remarkable fact of the action of light upon surfaces of silver with the above-mentioned phenomena produced by contact, we can no longer doubt that light acts on all bodies, modifying them so that they behave differently in condensing the vapours of mercury. A similar experiment was made with copper during unfavourable weather. The copper was not well polished, and, consequently, the image produced by the mercurial vapours was faint, although clearly visible. By exposing the plate to the vapour of iodine the image became stronger, and this method was found useful in experiments with copper. A plate of clean mirror-glass was exposed in the same way to light, and the action was as plain as on the silver, if the glass were afterwards breathed upon, the image remaining visible for a long time afterwards. We may therefore assume that light acts on all bodies, and its influence may be tested by all vapours that adhere to the substance or act chemically upon it."

Robert Hunt's Views.—Although Robert Hunt recorded these experiments in his "Researches on Light," he does not seem to have repeated them as regards the direct action of light upon metallic silver, but to have paid more attention to Moser's experiments on the images produced by contact or proximity of dissimilar substances, and his theory of invisible light, as well as the effects of heat. Hunt's own experiments were chiefly carried out on copper plates, and led him to attribute Moser's results to calorific or thermic radiations rather than to light. Knorr, Karsten, Grove, and others seem also to have investigated Moser's theories, but again without taking notice of the fact of images, either directly visible or developable, being produced on metallic silver by the direct action of light.

I have not been able to find a record of a visible action of light upon ordinary silver plate, though its occurrence should be well known to silversmiths.

Carey Lea's Observations.—Carey Lea found that the three forms of allotropic silver he obtained were all sensitive to light: A, the red soluble, and B, the dark brown or blue insoluble variety, becoming brown after some hours' exposure, while C, the golden coloured, became lighter by exposure (*Phil. Mag.*, 1891, Ser. 5, vol. xxxii., p. 337).

Electrolytically Deposited Silver.—In a series of electrolytic experiments made in Calcutta in 1892, I found that a golden-yellow or light olive-coloured deposit of silver on the cathode plate (silver or platinum) of a decomposition cell formed with two pure silver plates, as anode and cathode, or with a silver anode and platinum cathode in distilled water, through which a weak current was passed, was slightly sensitive to light, and became lighter in colour by exposure. This seems to confirm Carey Lea's observation, if my golden-yellow silver deposit was analogous to his C-product. My deposit being made by electrolysis of pure silver in fairly pure distilled water must have been nearly pure silver, with no traces of foreign substances beyond those contained in the silver or the water, unless there was a small amount of occluded hydrogen, which other experiments of the same series, but with a stronger current, showed might not be impossible.

Photo-electrical Observations in Calcutta.—In another series of observations on the electrical action of light upon silver made in Calcutta about the same time, and published in the *Journal of the Asiatic Society of Bengal*, Part II., No. 1, for 1893, I found that the action of bright sunlight on a plate of almost pure silver, as indicated by a very sensitive Rosenthal galvanometer, was to make the exposed half positive to the unexposed, or as zinc to copper, which would seem to point to some slight oxidising action. The observation, however, was a difficult one, not readily repeated with certainty, and no very definite result was obtained. The currents observed did not appear to be due to unequal heating of the two halves

of the plate, because the direct application of heat to the exposed side produced at once a clearly marked current in the opposite direction. This effect was always the same, and could be readily repeated.

In further observations of the same series, in which pairs of pure silver plates were partly immersed in distilled water or good tap water, one plate being exposed to light while the other was covered, as in Becquerel's electric actinometer, the current in nearly all cases, though small, was as above, the exposed plate being positive to the unexposed, as it generally was when the silver plates were placed in dilute sulphuric, nitric, phosphoric, or hydrochloric acids.

Confirmation of Moser's Observation.—Recent observations of the action of light upon silver, made in connection with the working of the Daguerreotype process, have fully confirmed Moser's observation quoted above, and shown that silver, when exposed under ordinary conditions, shows distinct sensitiveness to light, and that not only can an invisible developable image be obtained, as was done by Moser, but by prolonging the exposure printed-out impressions are produced which are clearly visible after exposure. The difficulty is to make sure of obtaining a surface of pure silver, free from the presence of condensed gases or other foreign matter which might affect the plate and give it a sensitive surface. The silvered glass plates used have generally been cleaned and polished with well-washed tripoli, and the metal plates in the same way, sometimes after being well cleaned with fine emery paper, and, in some cases, after making the metal red-hot.

Various Silver Surfaces Sensitive to Light.—Repeated observations with silver surfaces of different kinds, pure silver plates and foil, silver leaf on varnished glass, Daguerreotype plates and silvered glass, have shown that by an exposure in bright sunshine of about half-an-hour to one or two hours, under an ordinary black and white negative or a cut-out design, photographic images can be obtained, which are sometimes clearly visible after exposure, especially if it is at all prolonged.

Development of Images on Plain Silver Plates.—Whether visible or invisible, these images can be developed by the vapour of mercury, or by ordinary physical development with acid solutions of ferrous sulphate or pyrogallol acid, to which a little silver nitrate is added, as in the old wet collodion process. The images were also produced when the negatives or cut-out masks were separated from the silver surfaces by sheets of thin mica, which, as Dr. W. J. Russell, F.R.S., has shown, stops the action of vapours upon a sensitive gelatine dry plate, and no doubt would do so upon a silver plate. As a rule the mica itself makes no difference in the action of light, and is quite transparent to it, though, in some cases, it may exercise a slight retarding action. It was found, however, that when the silver surfaces were exposed to light in hydrocarbons, such as fluid paraffin, benzole, turpentine, &c., no action took place under the parts screened by mica, though the fluids were perfectly clear and colourless. Under ordinary conditions of exposure in a printing frame the mica appeared to exercise no special influence upon the plates, except at the cut edges, as will be noticed further on.

Effects of Pressure.—That the images were not produced by differences of pressure was proved by leaving the mica screen, with the cut-out black paper design at its back, in contact with a polished silvered glass plate in darkness for twenty-four hours. There was no visible image, but on development with mercury vapour the mercury was deposited fairly evenly all over the plate, except just where the outside edges of the mica and the edges of some initials cut in it had been in contact with the silver. Here there was very little deposit, and the edges appeared as dark lines on a white ground. There was no sign of the black paper design. The fact that the images were readily obtained from ordinary black and white photographic negatives is further evidence against the results being due to pressure.

First Experiment with Silver Leaf.—My first experiment was made on the 14th August last with a piece of silver leaf laid down on a plate of glass coated with varnish, and exposed in the sun for a short time under a plain cut-out cardboard screen. On developing with mercury vapour a faint image was visible, the mercury having deposited on the part exposed to light.

Next day the experiment was repeated. A similar plate was exposed under a black and white gelatine negative of some lace for half-an-hour in bright sunshine. On developing with mercury a very distinct, though faint, image of the lace pattern was produced, the mercury again depositing on the parts exposed to light, as in Moser's experiment.

Effect on Polished Silvered Glass.—Thinking that these results might be partly due to some action of light upon the varnish underlying the silver leaf, a piece of polished silvered glass was exposed under the same negative for about an hour. Again a distinct image was developed with the mercury, but partly positive and partly negative. A somewhat similar result was obtained on another plate developed with the ordinary acid iron and silver developer already noticed.

Effect on Pure Silver Plate.—The next experiment was with a piece of nearly pure silver plate, carefully cleaned with "Globe" polish, and washed with benzene to remove all greasiness. After half-an-hour's exposure in dull sunlight and development with mercury, an image was produced similar to the two first on silver leaf, *i.e.*, the mercury had deposited upon the exposed parts.

These experiments with three different forms of silver surfaces and two methods of development, all giving results similar to those obtained by Moser, seemed at any rate to prove the correctness of his observation, and the sensitiveness of ordinary forms of silver to light.

With the exception of the first, the foregoing trials were all made with a black and white negative on glass. Others were then made with cut-out black paper screens and with like results.

Observation of Printed-Out Visible Image.—The first observation of an image visible on the silver surface after exposure and without any development was on a plate of nearly pure silver, cleaned with tripoli and ammonia, polished off with dry tripoli, and exposed on the 21st August for about half-an-hour in sunshine under a black paper cut out screen. The parts exposed to light appeared lighter than the unexposed, but on development the mercury was deposited upon the unexposed parts. In this case the surface may have been affected by the ammonia used in cleaning, but it is also likely that the black paper used for the mask exercised some effect, as was afterwards found to be the case.

Another silver plate exposed for the same time under the same cut-out mask, but separated from it by a sheet of mica, did not show the visible image after exposure, though an image was readily developed with mercury vapour.

A day or two later, on the 24th August, the same experiment was repeated upon a plate of silvered glass exposed in the sun for half-an-hour under the cut-out mask, with a mica screen between it and the silvered surface. The image of the black paper design could be faintly but distinctly discerned in a suitable light, again appearing dark upon a lighter ground. Development with acid iron and silver brought out clearly the images of the paper mask, and of some letters cut out of the mica screen, as well as the edges of the mica screen itself.

A piece of silvered glass was then exposed for forty-five minutes under the same black and white negative as used in the first experiments, the silvered surface being protected from contact with the negative by a mica screen. In this case also a faint image was visible after exposure.

Several other prints, both from the lace negative and the paper masks, were made on silvered glass with longer

exposures, so as to obtain a distinctly visible image, and it was then found that there was a tendency to reversal of the image when developed with mercury vapour, *i.e.*, the mercury deposited upon the unexposed parts instead of upon the exposed. In one plate the image thus produced from the negative of lace, exposed for two hours in the bright August sunshine, has quite the appearance of an ordinary Daguerreotype picture on an iodised silver plate, though no halogen or other sensitiser was used.

Further trials of prolonged exposures of pure silver foil or plates, carefully cleaned with dry tripoli powder, have given very distinct printed-out images on the metal, so that there is no doubt about the fact that visible images can be produced on clean plain silver surfaces by light.

Blue Rays found to be Active.—In order to ascertain, if possible, what rays were active in producing these visible images upon the silver, and as it was hopeless to expect to obtain satisfactory results from observations with the solar spectrum, a slip of silvered glass was exposed under a small artificial spectrum of seven coloured glasses. After forty-five minutes' exposure in sunshine very faint images of the violet and cobalt blue glasses were distinguishable, but showed more distinctly when breathed upon. A similar result was obtained upon a pure silver plate, and on developing with acid iron and silver the space exposed under the cobalt blue glass developed out quite clearly, with traces of the violet and blue-green glasses. This result quite agrees with an observation made by Moser that only the blue and violet rays have any influence on pure silver, for he obtained very clear images by means of glasses of these colours, while only traces could be rendered visible when red glasses were employed, although they transmit more light and heat.

On another silvered glass plate, exposed under a similar colour screen or artificial spectrum, consisting of fifteen coloured glasses, for three hours in bright sunshine, the image has apparently reversed by over-exposure, the mercury being deposited on the spaces exposed under the red, orange, yellow, and yellow-green glasses, but not on those which were under the blue-green, blue, and violet glasses.

As we have seen, Robert Hunt was inclined to attribute Moser's results to the effect of heat or differences of relative temperature rather than to light or solar radiations, but his experiments were mostly carried out on copper, which is, as I have found myself, much more sensitive to rays of low refrangibility and to heat than silver is.

Developable Images Produced on Silver by Heat.—Towards the end of September, when the weather was much cooler than it had been at the commencement of my experiments in August, I found that there was a distinct falling off in the sensitiveness of the silver surfaces, and it seemed that Hunt's view might, at any rate to some extent, be correct. I therefore tried an experiment to see if the same developable images could be obtained by heat as by light. A silvered glass plate was polished and put into a printing frame with the cut-out paper mask and mica screen, in which were cut-out initials, just as if it were going to be exposed in the sun, but it was gently warmed for about five minutes over a spirit-lamp, and then developed with mercury. The cut-out initials and edges of the mica came out distinctly in dark lines, just as they did in the pressure experiment, but there was also a clear image of the black paper mask, which developed lighter than the ground, by the deposition of mercury, or the opposite of the ordinary action of light.

This is a very interesting observation, but recent repetitions of it with silvered glass plates and clean silver foil have quite failed to give such a distinct image of the black paper, though traces of it have been visible, and the edges of the mica and of the cut-out initials were always clearly impressed. In one case, when the silver foil was well heated to redness on both sides before being placed in the printing frame and the subsequent heating, no image of the initials was obtained, and only part of one edge of the

mica screen with a faint trace of one corner of the paper mask where there was extra pressure. From this it would seem that heat does not play any active part in the production of the images, though the higher temperature of the summer sunshine, as well as its greater actinic power, may accelerate their formation by light. This is, to a certain extent, proved by the fact that the most perfect printed-out image obtained on a pure silver plate was exposed for three days at the end of September, when the thermometer exposed in the sun at the same time did not rise above 64° F., so that there could have been no question of heat producing the effect, as there might have been under the hot, clear sunshine of August.

Protection from Air.—In most of the experiments the plates were protected by glass during exposure, so that the outer air had no direct access to them. When plates were exposed under mica screens and without the protecting glass, the outside unprotected surface became distinctly yellow and tarnished with long exposures.

Under Surface of Silvered Glass Plate not Sensitive.—In order, however, to ascertain the effect of cutting off all atmospheric action on the exposed side, a silvered glass plate was exposed from the back or glass side under a cut-out mask made of thin aluminium sheet, and exposed for four days in October, two days being sunny and two cloudy. There was no visible image on either side of the plate after exposure, but breathing showed an image on both sides. The plate was then developed with acid iron and silver, and showed the image not very distinctly, but as development was prolonged traces of it appeared at the back of the silver film quite clear of deposit, so that apparently the developer had worked through the protected parts of the film, while the exposed part had taken the deposit of silver. When the plate was dry there was, curiously enough, no trace of the image on either side of the plate.

This experiment was repeated in January, two silvered glass plates being exposed face to face for fifteen days, of which five or six were sunny and the rest fairly bright, with the object of also seeing whether an impression could be made through the upper plate on to the silvered surface of the under one. On developing with mercury a fairly clear image of the cut-out design was obtained on the inner surface of the exposed plate, dark on a lighter ground, but neither on the outer exposed silver surface of the upper plate, nor on the silvered surface of the lower plate was there any trace of an image. The experiment was repeated with a similar result. The only other case in which images have been obtained through the silvered film was on a plate partly fumed with hydrogen peroxide and developed with mercury, but much overdone. As far as they go, the experiments show that the visible image is not produced on the silver except more or less in contact with the air. Further trials in bright sunny weather are required to prove this.

(To be continued).

THE CRYSTALLINE STRUCTURE OF METALS.* (SECOND PAPER.)

By J. A. EWING, F.R.S.,
Professor of Mechanism and Applied Mechanics in the University
of Cambridge,
and W. ROSENHAIN, B.A.,
1851 Exhibition Research Scholar, Melbourne University.

THE investigations described in this paper deal principally with the phenomena of annealing. The first section of the paper describes experiments made in the hope of observing under the microscope the process of re-crystallisation in strained iron. It is well known that re-arrangement of the crystalline structure of iron occurs when the metal is heated to redness, and it is believed

that such changes are associated with the evolutions of heat which are indicated by "arrest points" during the cooling of iron. We hoped that by keeping a polished and etched surface of the strained metal under microscopic observation while the specimen was gradually heated, we should see a more or less sudden change in the crystalline pattern at a temperature corresponding to one of the "arrest points." This attempt, however, to watch the process of re-crystallisation failed, although the experimental difficulties of keeping a specimen under microscopic observation while it was being heated were successfully overcome. The specimen was electrically heated in a vessel with a thin glass or mica window, and the microscope-objective was kept cool by directing a strong blast of cold air on it and on the surface of the window. In one set of experiments the specimen was kept in an atmosphere of pure hydrogen during the heating, but it was found to become so much tarnished as to obliterate the crystalline pattern. At a red heat, however, the uniform luminous surface of the specimen was seen to develop a number of dark patches which, on slightly raising the temperature, spread over the entire field. No corresponding change was visible during cooling, but the phenomenon would recur every time the specimen was heated, provided it had been cooled below redness after the previous heating. This phenomenon was absent when the specimen was heated in a vacuum, and we believe that it indicates a chemical action between hydrogen and iron, possibly corresponding to the hydrogen arrest point discovered by Sir W. Roberts-Austen.*

In the next series of experiments the specimen was heated in a vacuum. On prolonged heating the specimen still became tarnished, but at first the crystalline pattern remained visible up to a bright red heat. No change in the pattern was observed, but subsequent polishing and etching of the same surface showed that a real change of crystalline structure had occurred. The original etched pattern on the surface had persisted after heating, simply because the differences of level and surface texture on which it depended had in no way been disturbed by the re-crystallisation. Any crystalline pattern seen under the microscope, whether it be produced by etching or relief polishing, consists either of coloured surface deposits, or of steps, or pits, or other differences of level in the surface, and these differences of superficial texture, like mechanical scratches, are not affected by re-arrangement of the crystalline elements. Coloured surface deposits would also remain unaffected. All attempts to observe the actual process of re-crystallisation must therefore be unsuccessful.

The next section of the paper deals with the changes of crystalline structure which go on in lead and other metals at comparatively low temperatures. Our attention was directed to this by noticing that a piece of plumber's sheet lead, when etched with dilute nitric acid, exhibits a strikingly crystalline structure, with large crystals. The character of this appearance led us to the view that a slow process of annealing or re-crystallisation was at work in such lead at ordinary atmospheric temperatures, and we have satisfied ourselves that this is the case. The method of investigation consisted in taking a series of micro-photographs, at low magnifications, of certain marked areas in the surface of a specimen, in order to watch the change which went on through lapse of time, or after application of some thermal treatment. It was necessary, for the reasons given above, to re-etch the surface before each photograph was taken.

We have observed that when a piece of cast lead is severely strained by compression, the originally large crystals, after being considerably flattened, are driven into and through one another, so that the etched surface of a strained specimen presents a fine grain, whose crystalline nature only becomes apparent under considerable magnification (80 to 100 diameters). A piece of lead severely

* Abstract of a Paper read before the Royal Society, May 31, 1900.

* Alloys Research Committee Report (*Proc. Inst. Mech. Eng.*), 1899.

strained in this way, and kept for nearly six months in an ordinary room without any special thermal treatment, was found to be undergoing continuous change during that time. A series of photographs of this specimen, taken at intervals during the six months, show that a great number of the small crystals have grown larger at the expense of their neighbours. In similar specimens which have been kept at 200° C., the growth has been much more rapid and more pronounced. The rate of growth is a function of time and temperature, but some specimens show much more rapid changes than others under similar conditions of temperature; in some cases five minutes' exposure to a temperature of 200° C. is sufficient to alter the crystalline pattern completely. Experiments have also been made at 100° C. and 150° C., leading to the general result that crystalline growth will occur at any temperature from that of an ordinary room, *i. e.*, 15° C. or 20° C., up to the melting-point of lead, and that in general the higher the temperature the more rapid is the initial rate of change. No numerical data can be given, as the crystals are quite irregular, both in size and shape. So far as our observations go, they lead to the result that when such crystalline growth has continued for some time at a given temperature, the structure becomes more or less stable, so far as that temperature is concerned, but exposure to a higher temperature may cause further growth to occur.

A comparison of micro-photographs of the same specimen at various stages reveals the fact that the growth of an individual crystal occurs, not in uniform layers all round it, but by the formation of arms and branches that invade the neighbouring crystals, the intervening portions sometimes changing at a later stage. This action is analogous to the formation of skeleton crystals in a metal during solidification from the liquid state, the space between the branches filling in as solidification proceeds.

A marked feature observed in several specimens was the large and rapid growth of one or two individual crystals; in several instances such individuals grew until they were some hundreds of times larger than their neighbours. We have not been able to discover the determining cause of such growth, nor, in general, why one crystal should grow at the expense of its neighbour. Generally the most aggressive crystals were found near the edges of the specimen. It is noticeable that at times a crystal which has already grown considerably is swallowed up by a more powerful neighbour.

Some light is thrown on the nature of these actions by the fact that this growth only occurs in crystals that have been subjected to severe plastic strain. By casting the metal in a chill mould, specimens of lead can be obtained having a crystalline structure quite as minute as that found in a severely strained specimen, but this structure remains unchanged at temperatures which produce rapid change in a strained specimen.

The investigation of the effects of such comparatively moderate temperatures was extended to other metals, *viz.*, tin, zinc, and cadmium. In tin, the various phenomena of crystallisation from the fluid state are strikingly illustrated on a large scale by the thin layer of that metal which constitutes the surface of commercial tin-plate. The effects of rapid and slow solidification in producing small or large crystals respectively are well marked, and an examination of the etched surface of tin-plate under the microscope reveals beautiful geometrical markings or pits, whose orientated facets produce the well-known selective effect of oblique examination. The study of the crystalline structure affords an explanation of the nature and method of production of patterns in "*moirés métallique*," a process which has long been in use for the decoration of articles manufactured of tin-plate.

In tin, also, we find that the smallest structure obtainable by quenching the melted metal in water remains unchanged at all temperatures up to the melting-point; on the other hand, specimens whose crystalline structure has been modified by great plastic strain exhibit phe-

nomena of re-crystallisation at lower temperatures similar to those observed in lead. In a piece of strained tin, an hour's exposure to 150° C. produced complete re-crystallisation. Exposure to lower temperatures for this short time produced no visible change, but we have not investigated gradual time effects in this metal. The behaviour of strained zinc and cadmium is analogous to that of tin and lead. Exposure to 200° C. is sufficient to produce rapid re-crystallisation in both zinc and cadmium. This is particularly marked in the case of ordinary sheet zinc. On etching commercial sheet zinc, no large crystals are visible. In this state the metal is strong and tough, bending quite noiselessly. After exposure to 200° C. for half-an-hour, it shows on etching a large brilliant structure, and the metal is then weak and brittle, and, when bent, breaks along well-marked cleavage planes and emits a "cry" like that of tin.

In cadmium the re-crystallisation is comparatively slow at 200° C., and a time effect has been observed; the action is rather different from that observed in lead. In cadmium the size to which the crystals grow appears to be much more uniform; no arms or branches are thrown out and no twin lamellæ are found.

The final section of the paper deals with an hypothesis, which is advanced as an attempt to explain the mechanism of the growth of crystals in apparently solid metal.* According to this hypothesis, the metallic impurities which are present in a metal play an important part in the action. When a metal solidifies from the fluid state, the metallic impurities ultimately crystallise as a film of eutectic alloy in the inter-crystalline junctions; when fairly large quantities of such eutectics are present, the microscope reveals their presence as an inter-crystalline cement, such as that formed by "pearlite" in slowly cooled mild steel; very minute quantities of eutectic, however, will be invisible and yet capable of forming a thin film of fusible cement. We conceive that the changes of crystalline structure which go on while the piece is in the solid state are accomplished by the agency of eutectic films between the crystals, in dissolving metal from the surfaces of some crystals and depositing it on others. When a metal is severely strained, these films of eutectic will be also strained and in many places broken, thus allowing the actual crystals to come into contact with one another. The difference in the rate of etching of adjacent crystals and the phenomena of the electrolytic transfer, in an acid solution, of lead from one crystal to another in the same mass of metal, support the supposition that there is a difference of electric potential between the crystal faces which are brought into contact by severe strain. If it be assumed that a film of eutectic alloy when fluid, or even when in the pasty condition that precedes fusion, can act as an electrolyte, we may regard any two crystals thus in contact, with a film of eutectic interposed in places, as a very low-resistance circuit, and the growth of the positive crystal at the expense of the negative would result. Moreover, such growth would be more rapid at higher temperatures, and its rate at a given temperature would vary in different specimens according to the nature and quantity of the impurities present. That an alloy can act as an electrolyte has not been established experimentally, but the assumption is supported by the close general analogy between alloys and salt solutions. This analogy extends to the very question of the growth of crystals, as Joly has shown that when crystals of a salt are immersed in their mother-liquor, growth of one at the expense of others will take place.

It should be added that solution of one crystal into the intervening film of eutectic, along with deposit on the neighbouring crystal from the eutectic, may occur as a consequence of differences of orientation, producing differences of "solution pressure" apart from actual electrolysis, but the fact that growth has not been ob-

* It is proper to say that this hypothesis is due to Mr. Rosenhain.—J. A. E.

served to occur except in strained crystals favours the view that the action is electrolytic.

Some further results which have been deduced from the above hypothesis have been verified by experiment. It follows from the hypothesis that an inter-crystalline boundary containing no eutectic would be an impassable barrier to crystalline growth, but if the eutectic could in any way be supplied, growth across the boundary might take place. In an absolutely pure specimen of lead there would be no eutectic at the inter-crystalline junctions, but as extremely minute traces of impurity would suffice to set up the action it is almost hopeless to verify the hypothesis in this way. Some experiments on the cold welding of lead have, however, borne out our conclusions. Two clean, freshly scraped, lead surfaces will unite under great pressure in the cold state, and if a piece so welded be annealed, we find that the crystalline growth due to the annealing, with very rare exceptions, never crosses the inter-crystalline boundary formed by the welding surface. To test whether the presence of some eutectic would allow growth to take place, we have scattered small quantities of a more fusible metal over the freshly scraped surfaces of lead before squeezing them together. Then, after a cold weld had been made by pressure, on annealing by exposure to 200° C. it was found that crystal growths frequently crossed the line of the weld, as the above theory led us to expect. This experiment has been repeated many times with the uniform result that whenever a small quantity of eutectic, or of an impurity capable of forming a eutectic with the lead, was scattered over the clean surfaces before welding a distinct growth of crystals across the boundary took place as a result of annealing. On the other hand, a large number of welds were made without introducing any impurity, and with very rare exceptions they showed no growth across the boundary, even after the annealing process was continued for some weeks. In rare exceptions a minute amount of growth across the boundary was observed, but these may fairly be accounted for by the almost unavoidable presence of traces of impurity. The result as a whole goes far to confirm this solution theory of crystalline growth in annealing.

THE COMPOSITION OF SOOT FROM MINERAL COAL.

By H. WARTH, D.Sc.

THE soot which is removed in large quantity from the chimneys of ordinary fire-places in which coal is burnt appears to be, at least in Birmingham, quite a commercial article on account of its value as a fertiliser. This made me enquire about the proportion of ammonium salts which it might contain. On turning to a chemical handbook, I found it stated that no data are available as to the composition of soot from mineral coal. I therefore made the examination following:—I selected a sample of the soot which had been collected from an ordinary household chimney under which coal had been burnt, said to have come from Cannock and Rugeley colliery, Hednesford. The sample weighed 368 grms. I first extracted the soluble matter by boiling with water, filtering, and evaporation. The product of evaporation was strongly hygroscopic, and in order to purify it still further I sublimated it, so as to obtain the ammonium salts separately as sublimate. The remainder was lixiviated with water and filtered, so as to obtain the soluble fixed (non-volatile) salts separated from carbon, &c.

The following quantities were obtained:—

	Percentage of salts from the original soot.
Ammonium sulphate	0·1
Ammonium chloride	7·3
Total ammonium salts	7·4
Total soluble fixed salts	1·3

These fixed salts consisted of sulphates and chlorides of sodium, magnesium, calcium, and iron. The fixed salts contained much more sulphate than chloride. The proportion may have been about three of the former to one of the latter. This explains the almost total absence of sulphate amongst the volatile portion. The sulphur trioxide was chiefly retained by the non-volatile metals, and thus it is that the volatile portion consists of nearly pure ammonium chloride. The proportion of ammonium salt in the soot is large enough to justify the estimation in which the soot is held as a plant manure.

Birmingham, June 22nd, 1900.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART III.

By HARRY BREARLEY.

(Continued from vol. lxxxii., p. 77).

CARBON.

PAPERS on the relation of carbon to iron, its mode of existence after various kinds of physical treatment, &c., have been almost entirely neglected.

The processes for estimating CO₂ in various solid, liquid, and gaseous compounds and mixtures have also been neglected, either because they are more properly treated in another section, or are of only second-rate interest in the steel works laboratory. For a like reason, a large number of papers on organic analysis—of which the estimation of carbon after its separation from iron is but a particular case—are not referred to. These omissions are not intended to suggest what may and what may not be neglected in an analyst's equipment. Some such omissions were, however, necessary in a compilation which aims at making each reference bear directly on the practice of steel works laboratories.

The following is the classification adopted:—

I. DIRECT COMBUSTIONS.

- a. Dry Way.
- b. Wet Way.

II. MODES OF RELEASING THE CARBON.

III. ESTIMATING THE LIBERATED CARBON.

- a. By Weighing the Dried Residue.
- b. Dry Combustion of the Residue.
- c. Wet Combustion of the Residue.
- d. Volumetric Estimation of the Residue.

IV. COLORIMETRIC ESTIMATION.

- a. Eggertz Process and Modifications.
- b. Tintometers and other Apparatus.

V. OTHER PROCESSES OF ESTIMATING CARBON.

VI. ESTIMATION OF GRAPHITE.

VII. MISCELLANEOUS NOTES.

The journals referred to are the same as in Part II., including the volumes completed in 1899.

I. DIRECT COMBUSTION OF THE SAMPLE.

a. In the Dry Way.—

307. MULDER (C. N., v., 5 and 210).—Cast-iron mixed with pumice stone is burned in oxygen. Regnault's mixture of KClO₃ and PbCrO₄ does not liberate chlorine.
308. HERMANN (C. N., xl., 263).—Direct combustion in O in a short platinum tube. The Fe₂O₃ formed verifies completeness of the combustion.
309. FÖRSTER (Z. I. S. I., 1895, ii., 588).—Ignite with PbCrO₄ in small porcelain retort. Large pieces of iron are oxidised more readily than very fine powder.
310. LORENZ (Z. C. S., lxiv., ii., 291; and lxvi., ii., 119).—Mixture of steel and PbCrO₄ ignited to white heat in oxygen.

311. LJUBAVIN (C. N., lvii., 221).— PbCrO_4 may evolve CO_2 on ignition; it should be fused in a Cu crucible.
312. PETERSSON (J. I. S. I., 1890, ii., 852).—Steel decomposed with KHSO_4 ; CO_2 and SO_2 absorbed in NaHO and $\text{Ba}(\text{HO})_2$; SO_2 oxidised to SO_3 , and CO_2 liberated with acid. Graphite is collected in a Pt funnel and burned in air and nitrous fumes. Later (J. I. S. I., 1893, ii., 527), SO_2 is retained by CrO_3 and gases passed over CuO into $\text{Ba}(\text{HO})_2$.
313. SCHNEIDER (J. I. S. I., 1894, ii., 488).—The filings are indirectly oxidised by igniting with metallic Pb or Cu. Carbide carbon is separated from iron with very dilute H_2SO_4 . Later (J. I. S. I., 1896, i., 531), purified phospho copper is used instead of powdered Cu.
314. BREARLEY and LEFFLER (C. N., lxxv., 241, 263, &c.).—Carbon in ferro-chromium can be estimated by igniting with PbCrO_4 , CuO , or PbO_2 . PbCrO_4 and CuO require high temperatures, PbO_2 does not.
315. ROZYETTI (J. S. C. I., 1899, 865).—Direct ignition of fine steel borings or powdered ferro-chromium with pure Al_2O_3 ; the process completed in thirty-five to ninety minutes.
316. SANITER (C. N., lxxv., 287 and 311).—Ignites with a mixture of litharge and CuO .
317. PARRY (J. I. S. I., 1880, 442).—Has always been able to detect CO in steel. (Would this heighten the results obtained by direct combustion?—H. B.).
318. FUNK (J. C. S., lxx., ii., 274).—The C in Zn is determined by direct combustion in oxygen.
- I.b. In the Wet Way.*—
319. JUPTNER (J. I. S. I., 1883, 779).—The sample is digested with CrO_3 and a large amount of H_2SO_4 . The evolved gases are dried and passed through KHO.
320. GMELIN (J. I. S. I., 1885, 246).—Very much like Juptner's process.
321. HEMPEL (J. I. S. I., 1895, i., 503).—Decompose sample with CrO_3 and H_2SO_4 in the presence of Hg; measure the CO_2 evolved, after exploding in a pipette to destroy hydrocarbons. No hydrocarbons are evolved on treating grey pig-iron.
322. WIBORG (J. S. C. I., 1887, 748; and 1890, 768).—Treat Fe with CuSO_4 , and, without filtering, oxidise C with $\text{CrO}_3 + \text{H}_2\text{SO}_4$; measure CO_2 in tube. The deposited Cu protects Fe from acid until a high temperature is reached: at lower temperatures hydrocarbons are evolved.
323. VON REIS (J. I. S. I., 1888, i., 376; and 1889, ii., 475).—Describes and commends Wiborg's process.
324. JUPTNER (J. C. S., lvi., 186).—Describes Wiborg's process.
325. LUNGE and MARCHLEWSKI (J. C. S., lxiv., ii., 45; lxv., ii., 188; and J. I. S. I., 1894, ii., 484).—Modified Wiborg process. H_2O_2 is used to generate O in the liquid, so as to expel CO_2 . Separation of Fe with Cu solution and wet combustion of residue inaccurate (see also J. C. S., lxii., 531).
326. DONATH and ERLLENHOFER (J. I. S. I., 1897, ii., 496).—A modification of Wiborg's process.
327. REINHARDT (J. I. S. I., 1892, ii., 511).—Gases burned to CO_2 by passing over electrically heated Pd spiral, and measured over Hg. Later (J. I. S. I., 1893, i., 403), uses heated platinised asbestos or prepared pumice.
328. BLAIR (J. C. S., lxx., ii., 544).—A modified Wiborg process. Combustion made with $\text{CrO}_3 + \text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$, and CO_2 measured over Hg.
329. ROUFF (J. S. C. I., 1899, 176).—Sample decomposed with CuSO_4 and a mixture of sulphuric, chromic, and phosphoric acids. The evolved CO_2 is measured. Not so good for ferro-alloys as for steels.

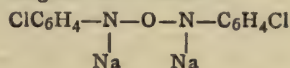
330. CAMPREDON (J. S. C. I., 1898, ii., 84).—Uses Wiborg's process after separating the C or graphite.
331. KOCH (J. S. C. I., 1894, 979).—Like Juptner, but passes gases over hot CuO . Special apparatus illustrated. (See also WUST, J. C. S., lxx., 449).
332. VON REIS (J. I. S. I., 1894, ii., 485).—Hydrocarbons are given off from direct combustion with CrO_3 and H_2SO_4 ; H_2SO_4 absorbs them; therefore dries with phosphoric anhydride instead. Addition of CuSO_4 lessens evolution of hydrocarbons. A constant error of 2 per cent is allowed for. (See also J. I. S. I., 1888, i., 374). Pumice moistened with KHO a better CO_2 absorbent than KHO bulb.
333. WOOD (J. S. C. I., 1884, 652).—Decompose sample with acid, pass gases through H_2SO_4 , alkaline Pb solution, and combustion tube into KHO.

(To be continued).

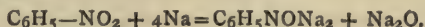
THE REDUCTION OF NITROBENZENE BY SODIUM.

By JULIUS SCHMIDT.

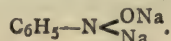
By reacting with metallic sodium on parachloronitrobenzene in ethereal solution, A. Hoffmann and A. Geyger obtained a very unstable black substance, to which, under reserve, they assigned the formula—



They did not succeed in preparing an analogous metallic compound with nitrobenzene, and they assume that sodium has no action on this nitrated hydrocarbide under these conditions. The author of this paper, who has repeated the experiments of the above-mentioned chemists, has found that, contrary to what they state, a reaction does occur at the ordinary temperature, between the sodium and the nitrobenzene, conforming to the following equation:—



The new compound which is thus formed may be regarded as a bisodic derivative of β -phenylhydroxylamine—



According to the author the reaction takes place much more energetically if, instead of operating at the ordinary temperature, the sodium is added to a boiling solution of nitrobenzene in toluene. The supposed bisodic substance occurs in the form of a blackish-brown powder possessed of a very considerable reducing power.

Decomposition of the Product of the Reaction under the Influence of Dilute HCl.—By treating the compound in question with double normal hydrochloric acid, a transformation takes place which gives rise to the formation of phenylhydroxylamine.

Slow Oxidation of the Product in the Air.—If we pass a current of dry air through cold ether containing the blackish-brown bisodic derivative in suspension, this latter gradually takes a brick-red colouration, and after the lapse of several hours is no longer capable of reducing an ammoniacal solution of silver, or Fehling's solution. If it is then treated with dilute H_2SO_4 , CO_2 is given off, and, by distillation of the acid liquor with steam, we obtain orthonitrophenol.

Oxidation of the Sodio Derivative with the Aid of Bichromate of Potassium and Sulphuric Acid.—By submitting the product to the action of this oxidising mixture, the author has obtained a compound, which he was able to recognise as nitrosobenzene, by its crystalline structure, its fusing-point (68°), and its odour.—*Berichte*, xxxii., p. 2911.

ON

CRYSTALLISED SELENIDE OF MANGANESE,
AND ON AN OXYSELENIDE.

By M. FONZES-DIACON.

FUSED selenide of manganese has been prepared by M. Fabre, by the action of selenium fumes on manganese heated to redness. This author has also obtained an amorphous reddish-grey selenide of manganese by the wet way.

I have prepared this body in a well crystallised form, both by the wet and dry way.

By the Wet Way.—Seleniuretted hydrogen precipitates a solution of acetate of manganese, giving, if the current passes slowly, a blackish-grey selenide, which is first deposited, followed by an orange-yellow selenide which forms a second layer, quite distinct from the first.

The blackish-grey selenide is crystalline, the yellow selenide is amorphous. If we add a small quantity of hydrochloric acid to the solution of acetate of manganese, and then saturate it with a current of seleniuretted hydrogen, the precipitation is not complete, but after two or three weeks a blackish-grey crystalline precipitate is formed, which under the microscope consists of beautiful non-modified cubes.

This selenide, dried in hydrogen to prevent its easy decomposition by air, has the formula $MnSe$.

Solutions that are too strongly acid are not precipitated by seleniuretted hydrogen; if the precipitation is carried out without proper precautions, we obtain a reddish-grey selenide of manganese, made up of a mixture of black crystalline selenide and orange-yellow amorphous selenide.

By the Dry Way.—Seleniuretted hydrogen reacts at a dull red heat on dried chloride of manganese giving crystallised selenide of manganese. The boats contain a black mass with a brilliant blown-out surface; the bubbles are lined on the inside with fine grey prismatic needles, appearing yellow by transmitted light. These crystals, which answer to the formula $MnSe$, are of too small a size for their crystalline form to be accurately determined.

We can also prepare crystalline selenide of manganese by reducing by carbon, at the high temperature of the electric furnace, a mixture made in the proportion of 1 molecule of seleniate of manganese to 4 molecules of sugar charcoal. This mixture, kept for ten minutes at the temperature of an electric arc of 80 volts and 140 ampères, becomes transformed into an ingot of selenide of manganese having a crystalline fracture with a brilliant grey appearance.

The action of this high temperature prolonged for even half-an-hour does not drive off any selenium.

We can also obtain a similar selenide by melting precipitated selenide of manganese in a carbon crucible, placed in a Moissan furnace in such a manner that the bottom part is heated. After heating for ten minutes with a current of 80 volts and 140 ampères, we obtain an ingot with a metallic appearance having a crystalline surface, cleaving with the greatest ease in three rectangular directions, giving flakes appearing grey by transmitted light but having no action on polarised light.

This selenide, of the formula $MnSe$, is isomorphous with the sulphide of manganese obtained under the same conditions by M. Mourlot.

Finally, I have been able to prepare fused selenide of manganese by the aid of a very beautiful method which consists of removing the oxygen from the seleniate of manganese by means of aluminium.

Powdered aluminium is intimately mixed with dried seleniate of manganese in the proportions indicated by the formula $3SeO_4Mn + 4Al_2 = 3SeMn + 4Al_2O_3$. The powder thus obtained is placed in a crucible and ignited by means of a piece of burning magnesium wire without the necessity of heating it.

The reaction is extremely violent: a long jet of flame escapes from the crucible, and, if it is then covered with a lid held firmly on, the melted mass causes this lid to adhere to the edge of the crucible, which, under the influence of the intense heat given off, becomes almost white-hot.

After cooling the melted selenide of manganese is detached from the cover and the sides of the crucible; it is nearly pure, and only contaminated on the surface with a little alumina.

If we do not take care to hold the cover on firmly when once the reaction is commenced, the whole mass will be thrown out of the crucible.

Properties.—Crystallised selenide of manganese, prepared in the electric furnace, has a density of 5.59 at 15°. It is easily attacked, even by dilute acids; fuming nitric acid transforms it into selenite of manganese.

Gaseous hydrochloric acid easily caused the evolution of SeH_2 .

When reduced to powder and treated with boiling peroxide of hydrogen containing a little hydrochloric acid, it is transformed into selenite of manganese.

It burns in chlorine, giving $MnCl_2$ and $SeCl_2$.

Oxyseleide of Manganese.—When we attempt to reduce seleniate of manganese by hydrogen at a high temperature, we obtain a green powder mixed with black selenide of manganese; at the same time selenious anhydride is given off, and condenses in the cooler parts of the tube.

This green powder, roughly separated, dissolves in hydrochloric acid, giving off SeH_2 ; it burns in oxygen, giving SeO_2 and saline oxide of manganese. It is an oxyseleide, analogous to the green oxysulphide of manganese which is formed on reducing sulphate of manganese by hydrogen.—*Bull. Soc. Chim.*, Ser. 3, xxiii, No. 12.

LABORATORY NOTES.

By J. M. CAMP.

If apologies are required for the following notes, mine lie in the fact that they are detailed descriptions of some methods of analysis, partly new, that have stood the test of time and practical operations. They include a method for determining phosphorus in coke and coal, the determination of phosphorus in ores, pig-iron, and steel containing arsenic, and the determination of alumina as phosphate in ores and blast-furnace cinder.

PHOSPHORUS IN COKE AND COAL.

One of the requirements at the laboratory of which the writer has charge is the determination of the ash, sulphur, and phosphorus each day in an average sample of coke from all furnaces of the previous day's consumption. The fusion of the ash, consisting as it does of about 50 per cent silica, 30 per cent alumina, and 10 per cent sesquioxide of iron, with other bases, and its final evaporation to dryness to separate silica, is at best a tedious process which can not be safely hastened. The result is that the time of analysis is unduly prolonged; consequently the following scheme was evolved, yielding excellent results in the minimum of time.

The sample of coke partly dried, and ground to pass through a forty-mesh sieve, is delivered to the laboratory by the sampler on the afternoon of the day on which it is taken. This is dried at 100° C. for one hour, and when cool 5 grms. are weighed off into a 1½ inch porcelain crucible. This is left in the muffle furnace over night, and in the morning the lump of ash and any particles adhering to the crucible are transferred to a 30 c.c. platinum crucible, mounted on a platinum tripod. About 5 c.c. of dilute hydrochloric acid are now added, one acid to two of water, and about 10 c.c. of hydrofluoric acid, and the crucible and tripod are placed directly on the top of the chimney of an Argand burner, and the flame so regulated that the solution will not boil. In from 20 to 30 minutes

the solution is evaporated to dryness and dried to drive off the last traces of hydrofluoric acid, but not baked, as this will render some of the bases insoluble in the dilute acid to be subsequently used. When cool, about 15 c.c. of the same dilute hydrochloric acid are added, and the crucible warmed until all is in solution. The contents of the crucible are now transferred to a 12 c.m. evaporating dish, and 5 c.c. of strong nitric acid added. The bulk of the solution now aggregates about 75 c.c., and the solution is boiled for one or two minutes and then filtered, to remove any possible traces of silica or unconsumed carbon, into a sixteen-ounce flask.

The treatment now is the same as that previously described before this Society (*Proc. E. S. W. Pa.*, vol. xi, p. 251), to wit, the addition of 25 c.c. of strong ammonia, and then strong nitric acid until the precipitated iron and alumina are just dissolved, and then 5 c.c. in excess, making a total of about 25 c.c. strong nitric acid.

The solution is brought to 85° C. and 75 c.c. of molybdate solution, blown in by aid of a pipette, after which the solution is kept agitated for about five minutes, and is then filtered through a weighed filter-paper that has been dried at 115° to 130° C., and weighed between watch-glasses. The precipitate is washed with a 2 per cent solution of strong nitric acid, dried one hour at the above temperature, and weighed between watch-glasses; 1.63 per cent of its weight is taken for phosphorus.

In the case of coals the treatment is exactly similar, except that the coal is usually coked in a large platinum crucible, and then, to save the platinum crucible from the protracted heating, the coke is transferred to a porcelain crucible for complete combustion in the muffle preferably over night.

THE DETERMINATION OF PHOSPHORUS IN ORES, PIG-IRON, AND STEEL CONTAINING ARSENIC.

For the exact determination of phosphorus in ores, particularly manganese ores, coming as they do from all quarters of the globe, and in pig-iron or steel containing arsenic, although this impurity is not an every day occurrence, a method is very desirable wherein at some stage of the analysis the arsenic can be eliminated without a marked change in the essential details of the regular phosphorus determination, and without prolonging the time of the analysis beyond that of the regular routine work. Numerous experiments have been made by the writer along these lines, mainly in the attempt to reduce the concentrated ferric chloride solution to the ferrous state, and then volatilising the resulting arsenious chloride, but without marked success, until, acting on the suggestion contained in a paper by Mr. E. D. Campbell (*Journ. Amer. Chem. Soc.*, vol. vii.), describing briefly some experiments made by his students who used oxalic acid as the reducing agent, the following scheme was worked out. Excellent results were obtained up to 1 per cent arsenic. The method for ores only will be given; its application to pig-iron or steel will be readily seen.

Five grms. of the ground and dried sample are weighed off into a 12 c.m. porcelain dish with watch-glass cover, and 50 c.c. of strong hydrochloric acid added, and the solution boiled gently for about thirty minutes. It is now diluted with sufficient cold water to prevent cutting the filter-paper, and filtered into another dish of the same size.

This solution will contain all the unvolatilised arsenic in the ore, and it is placed on the steam-bath to go to dryness over night. The residue is burned and fused with the mixed carbonates, and the fusion allowed to harden around a platinum rod. The crucible is now warmed, and the greater bulk of the fusion removed on the platinum rod. This, while still hot, is placed in the dish with cover, in which the ore was originally dissolved, and containing 10 or 15 c.c. of water. Dilute hydrochloric acid is added to the crucible and warmed, and this process is repeated until all of its contents are removed and added to the dish containing the fusion. An excess of strong

hydrochloric acid is now added to dissolve any of the remaining fusion, and this dish is placed with the other on the sand-bath. In the morning, to the dish containing the dried mass from the original filtrate, 2 grms. of pure oxalic acid are added, and 50 c.c. of strong hydrochloric acid, and the solution, with watch-glass cover, evaporated to dryness by hard boiling, but not baked. When cool add 30 c.c. strong hydrochloric acid, and evaporate to first appearance of insoluble ferric chloride, remove from the light and add 10 c.c. strong nitric acid when the violent action has ceased, warm until all is in solution, dilute with cold water and filter into a sixteen-ounce flask, using 2 per cent nitric acid for washing. In the meantime, to the dish containing the fusion, dilute hydrochloric acid is added just sufficient to moisten, and enough hot water to dissolve the chlorides. This is warmed until all is in solution but the separated silica, and filtered into the same flask with the original filtrate. The phosphorus is now precipitated as above described for phosphorus in coke.

THE DETERMINATION OF ALUMINA AS PHOSPHATE IN ORE AND BLAST-FURNACE CINDER.

The greatest advantages which precipitating and weighing alumina as phosphate has over the hydrate precipitation is in ore analysis, where, with the latter method, the iron and alumina are weighed together, the iron being finally determined by solution of the precipitate and titration, or preferably titration in another portion of the same sample. All the errors of the entire manipulation are thus thrown on the alumina, the lesser dog. In the phosphate precipitation, however, the alumina is determined in a separate portion, and is responsible only for its own manipulative errors. In blast-furnace cinders, to determine the alumina, which is the laboratories' daily task, the determination of iron is entirely obviated. Most furnace managers are content to receive the silica and alumina in each day's cinders, counting the balance as bases, with a full analysis at regular stated intervals. The iron not being an essential component of the cinder, its determination in a cinder of a normal working furnace, where it is little more than a trace, is useless, while, with an abnormal working furnace, where it may be high, the manager has something else on hand to worry him of much more importance.

The filtration and washing of the phosphate precipitate are also much faster than the same operation with the hydrate precipitate. This statement applies particularly to cinders, where the large amount of alumina apparently coagulates the separated sulphur and precipitate settles rapidly, leaving the supernatant liquid practically clear and readily decanted. In ores, where there is much less alumina, more free sulphur is in suspension, and a partial but not aggravating clogging of the filter occurs.

One disadvantage of the phosphate method is that there is no end point to the washing of the precipitate, it being slightly soluble in the wash water, and after the tenth washing, showing with molybdate solution a fairly uniform volume of phosphomolybdate precipitate in equal volumes of the successive filtrates up to the twentieth washing. The addition of acetic acid and ammonium acetate to the wash water gave a slightly greater weight of aluminum phosphate from a slag of known composition, but still showed the phosphate in the filtrates up to the twentieth washing. It is important that the precipitate be washed thoroughly, otherwise the platinum ware, if used, will suffer.

The method as used on ore and cinders is as follows:—

To the cold hydrochloric acid filtrate from the silica of 1 gm. of ore or cinder diluted to about 400 c.c. in a No. 5 beaker, add 30 c.c. of a 10 per cent solution of ammonium phosphate and then ammonia until a faint permanent precipitate is formed; 1.5 c.c. of strong hydrochloric acid is now added, and for ores, on account of the greater bulk of iron present, 50 c.c., and for cinders 30 c.c. of a 20 per cent solution of sodium hyposulphite. The

beaker is now placed over the light and heated just to boiling. Now in the same graduate measure off 8 c.c. of strong acetic acid and 15 c.c. of a 20 per cent solution of ammonium acetate, and add to the boiling solution and boil ten minutes. If the latter is added before the solution is boiling, or near the boiling-point, the precipitate will be flocculent and difficult to filter. Remove beaker from the light and allow precipitate to subside, decant clear solution and wash precipitate on to the filter, and then wash ten times with hot water. Transfer precipitate to platinum crucible without lid and place in front part of the muffle; when paper is charred transfer crucible to hottest part of muffle till burned. Cool and weigh; 41.85 per cent of the weight is alumina.—*Proceedings of Engineers' Society of Western Pennsylvania*, xvi., No. 2.

NOTICES OF BOOKS.

A History of Chemistry from the Earliest Times to the Present Day. By ERNST VON MEYER, Ph.D. Translated, with the Author's sanction, by GEORGE MCGOWAN, Ph.D. Second English Edition, translated from the Second German Edition, with numerous Additions and Alterations. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1898. Pp. 631.

NOWHERE in antiquity do we find any endeavour to gain an insight into chemical processes by means of definitely planned experiments; though for hundreds, perhaps thousands, of years, chemical reactions have been used to attain certain ends, it was not until the first half of the sixteenth century, almost contemporaneously with the Reformation, that chemistry, losing its alchemistic tendencies, began to develop in a new direction.

In this "History of Chemistry" the author describes the development of chemical knowledge, and especially of the general doctrines of chemistry which have been gradually evolved from their earliest known beginnings up to the present day. In the general descriptions great emphasis has been laid upon the genesis of new ideas, and their gradual expansion into important dogmas or comprehensive theories.

In the special sections fundamental facts have been collected together, and these have been sifted and relegated to their proper branch of the science, thus forming as clear a description as possible of the state of chemical knowledge at any particular time.

The period of phlogistic chemistry was really an important one in the growth of the science; in spite of the false hypothesis which lay at the root of the theory, it was this theory, together with the work which resulted from it, that formed the foundation for the correct standpoints and researches of the succeeding period.

The latest period of chemistry, to which the present generation belongs, is closely associated with the name of Lavoisier, who turned the chemical science of his day into new paths; he demonstrated the supreme importance of the proportions by weight in chemical reactions: this applied more especially to the phenomenon of combustion and similar processes which Lavoisier was the first to explain correctly.

The next important step was the elaboration of the atomic theory founded by Dalton, which has gradually led up to Newland's and Mendeleeff's periodic system of the elements, Crookes's hypothesis of a primary material (protyle), and van 't Hoff's conceptions of the transformation and conservation of energy which have now come into general application in chemistry, more especially in the explanation of affinity-phenomena.

The enormous strides made in the science of chemistry in modern times is undoubtedly due to the greater facilities which have been available during the last few decades; the efforts made by Davy resulted in an increasing demand

for lectures with appropriate experiments. Practical instruction in chemical laboratories, as commonly carried out at the present day, was developed by Liebig; it was he who laid down the order in which the study of the various branches of the subject should succeed each other, and, thanks to the stimulus he exerted, a school was founded in his laboratory whose beneficial influence is felt at the present day all over the world.

The Carbonic Anhydride of the Atmosphere. By Prof. E. A. LETTS, D.Sc., Ph.D., and R. F. BLAKE, F.I.C., F.C.S. From the Scientific Proceedings of the Royal Dublin Society. Dublin: The University Press. 1900.

THE papers included in this number of the *Proceedings* of the Royal Dublin Society were read respectively on the 22nd June, 1898, and in April, 1899. The first paper deals with the methods of determining the amount of CO₂ in the air, with the authors' experiments on Pettenkofer's process as modified by them, and their experiments on the action of baryta water on glass and on silica, and the disturbing effect of soluble silicates on the delicacy of the phenolphthalein colour reaction.

Atmospheric carbonic anhydride, first shown to be present in the air by Dr. Black, of Edinburgh, probably between the dates 1752 and 1754, plays such an important part in nature, that the question of its amount, whether in the past, present, or future, is one of very great interest, not only to the chemist, but to the biologist, geologist, meteorologist, and student of nature generally.

The reciprocal action of plants and animals on air provides each with an important requisite, viz., carbon and oxygen respectively, and keeps in circulation the supply of carbon which is essential to the existence of both. If from any cause the amount of atmospheric carbonic anhydride should be largely increased, the existence of animals would be threatened, while if the reverse occurred vegetation would suffer, and animals would also stand in danger of eventual annihilation from the want of food, which they derive from the synthetic processes of the vegetable world.

This aspect of the question is considered in Part II., in which the causes of the variation of amount are studied, as well as the influence of day and night, vegetation, atmospheric precipitates, such as snow, fog, rain and mist, wind, the seasons, &c. Soil possesses the power of diminishing atmospheric carbonic anhydride at times, and then the air on the ground level contains less than that at higher levels; rain causes this, especially in the spring, that being the period when the soil is at its wettest. The volume, which will be read with great interest, concludes with a long and valuable list of the bibliography of the subject.

Elementary Practical Chemistry and Quantitative Analysis.

By FRANK CLOWES, D.Sc., Lond., &c., and J. BERNARD COLEMAN, A.R.C.Sc. Third edition. London: J. and A. Churchill. 1900. Pp. 282.

THE course of instruction given in this book is adapted to those students who do not need so thorough a chemical training as that which must be undertaken by one who has ambitions of becoming a professional and analytical chemist. The book is divided into two parts.

Part I. comprises a course of instruction on general chemistry, which gradually presents the principles of chemistry to the student by means of a selected series of experiments.

Part II. describes the analytical reactions of the commonly occurring elements and inorganic acid-radicles, and the methods of detecting them when they occur singly or in mixtures. At the end we find the usual tables for qualitative analysis, in which the elements are divided into the well-known groups and sub groups. Taken as a whole the book is sound, though not going very deeply into the subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

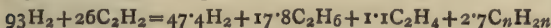
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 23, June 5, 1900.

Method of Decomposing several Metallic Perchlorides.—Echsner de Coninck.—The author finds that various perchlorides are decomposed by the action of animal charcoal. He experiments on gold and platinum tetrachlorides, also on iron perchloride, in dilute aqueous solution. Other chlorides, such as NiCl_2 , CoCl_2 , FeCl_2 , MnCl_2 , ZnCl_2 , CuCl_2 , and MgCl_2 , undergo no change. The author proposes to continue this research on the decomposition of iron perchloride.

Conditions of Stability of Rotatory Power.—J. A. Le Bel.—If, instead of operating with bodies at ordinary temperatures, a temperature of about 100° is employed, it is seen that four different radicles united to the carbon will be necessary, but not more than sufficient to cause the rotatory power to appear in sodium amylic alcohol and in bromo-succinic acid; this is because these bodies present, under such conditions, a remarkable instability, in the same manner as active bodies containing nitrogen. On the other hand, when no new atoms are introduced from a new species, the stability is always increased by increasing the volume of the radicles.

Dihydroxylates.—M. de Forcrand.—The author examines the action of dilute peroxides of hydrogen in various proportions of dissolved alkaline bases at a temperature of about 15° . Numbers are given for the bases soda, potash, lithia, ammonia, and monomethylamine, CH_3N .

Hydrogenation of Acetylene in presence of Copper.—Paul Sabatier and J. B. Senderens.—A mixture of acetylene and excess of hydrogen is passed over copper recently reduced with hydrogen and cooled in this gas. In the cold no permanent action takes place. Combination starts at about 130° ; a considerable amount of heat being evolved. The reaction taking place is probably represented by the equation—



By increasing the proportion of acetylene, the special action of copper on acetylene begins to be noticed, cuprene being formed.

Cuprous and Mercurous Organo-metallic Compounds of Diphenylcarbazone.—P. Cazeneuve.—In a preceding paper the author noticed the metallic derivatives of diphenylcarbazone corresponding to the general formula $\text{CO} \begin{smallmatrix} \text{NM}'\text{—NH—C}_6\text{H}_5 \\ \text{N} = \text{N—C}_6\text{H}_5 \end{smallmatrix}$. Under certain experimental conditions, the cuprous and mercurous derivatives

corresponding to the formulæ $\text{CO} \begin{smallmatrix} \text{NCu—NCu—C}_6\text{H}_5 \\ \text{N} = \text{N—C}_6\text{H}_5 \end{smallmatrix}$

and $\text{CO} \begin{smallmatrix} \text{NHg—NHg—C}_6\text{H}_5 \\ \text{N} = \text{N—C}_6\text{H}_5 \end{smallmatrix}$ can be obtained. These substances easily lose the metal, being transformed into carbodiazide, $\text{CO} \begin{smallmatrix} \text{N=N—C}_6\text{H}_5 \\ \text{N=N—C}_6\text{H}_5 \end{smallmatrix}$, a substance which has not yet been isolated, E. Fischer having only prepared the sulphocarbodiazine, $\text{CS} \begin{smallmatrix} \text{N=N—C}_6\text{H}_5 \\ \text{N=N—C}_6\text{H}_5 \end{smallmatrix}$.

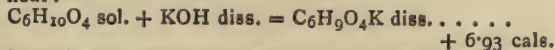
Acidimetry.—A. Astruc.—The author continues his researches on this subject, considering now the behaviour of various organic acids with regard to certain indicators. The special acids considered are isethionic, sulphanilic, meconic, and mellic acid.

Bulletin de la Société Chimique de Paris.

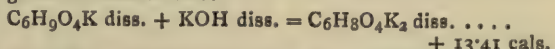
Series 3, Vol. xxxiii., No. 4.

Thermic Examination of Normal Adipic Acid.—

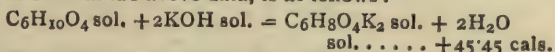
G. Massol.—The author has determined the heats of neutralisation and formation of the potash salts of normal adipic acid. This acid, when prepared and purified carefully, melts at 146.5° . It is anhydrous, and the acidimetric assay with phenolphthalein gave 100.2 per cent. The acid is too slightly soluble in water (1 per cent at 15°) for its heat of solution to be determined. The solution of 1 molecule of adipic acid in a solution of potash (1 mol. in 4 litres) is easily effected at the ordinary temperature, and produces a considerable quantity of heat:—



This figure represents the heat of neutralisation of the acid salt, less the heat of solution of the solid acid. The addition of a second molecule of potash to the acid salt gives the neutral salt:—

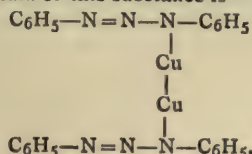


The total heat of neutralisation representing the formation of the neutral salt is $+20.34$ cal. The solution of adipate of potash, neutral to phthalein and litmus, gave the neutral anhydrous salt by evaporation and desiccation at 100° . This salt dissolves in water with the evolution of heat: 1 mol. (= 222 grms. in 1 litre) gives off $+2.67$ cal. The heat of formation of the solid neutral adipate, calculated from the above data, is as follows:—



This high figure shows that adipic acid is an energetic acid quite comparable with its homologues, succinic, glutaric, and suberic acids, which, under the same conditions, give off $+46.50$, $+44.23$, and $+44.76$ cal.

A Cuprous Salt of Diazoamidobenzene.—L. Meunier and A. Rigot.—To a very concentrated solution of diazoamidobenzene in alcohol, freshly prepared finely divided copper is added, and the mass well stirred for twelve hours. In this manner a yellowish-brown precipitate is obtained, which is washed with alcohol to eliminate the uncombined diazoamide. The residue which contains the excess of copper is exhausted with boiling benzene, which dissolves the organo-metallic substance. When evaporated, the benzenic solution leaves a residue formed of needles, which, after being purified by several crystallisations in boiling benzene, take the form of small yellowish-orange felted crystals, which may be dried at 50° . The formula of this substance is—



This cuprous salt is insoluble in water, alcohol, ether, and ligroin; it is slightly soluble in benzene, especially when heated; it decomposes at about 270° . Ordinary nitric acid decomposes it with explosion and incandescence. When a current of hydrochloric acid gas is passed through a benzenic solution of the cuprous compound, a yellowish-white precipitate is formed immediately, and the solution becomes colourless; this precipitate, collected and washed with ether, forms a bright yellow amorphous powder, soluble in water, in which solution sulphuretted hydrogen gives a precipitate of sulphide of copper, and nitrate of silver a precipitate of chloride of silver.

Some Amines containing the Camphor Radicle.—G. Blanc.—Already noticed in this column.

Rapid Method for the Estimation of Clay in Soils.—F. Poquillon.—Already inserted in full.

MISCELLANEOUS.

Estimation of Sulphur in Naphtha.—A. Lidof.—The author dissolves 1 grm. of naphtha in pure ether, and mixes it in a mortar with 30 grms. of a mixture of powdered NO_3K and Na_2CO_3 (17 parts of NO_3K and 13 parts of Na_2CO_3). After evaporating off the ether he throws the residue, a little at a time, into a large platinum crucible (250 to 300 c.c.) heated to redness. He then estimates the SO_4H_2 with BaCl_2 in the usual manner. Although a large part of the sulphur contained in the naphtha is in the form of volatile organic compounds, the method gives sufficiently exact results for ordinary practical purposes.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 567.

Methods of Preparing Graphitic Acid.—L. Staudenmaier.—The author gives two methods for the preparation of this body in small quantities as a lecture experiment. Then follows a process for the preparation of this acid on the large scale. For this purpose a well-powdered good quality graphite, such as commercial Ceylon graphite, is preferred; 250 grms. of this substance are treated with a mixture of 7 litres of sulphuric acid and 3 litres of nitric acid $\text{D} = 1.37$. After adding about 9 kilograms of powdered chlorate of potassium, the whole is left for six days at a low temperature; the supernatant liquid is then decanted, and the greenish product obtained is washed with warm water, then with nitric acid $\text{D} = 1.4$, diluted with one volume of water. The oxidation is finished by means of permanganate of potash and hot sulphuric acid, and the permanganic acid formed is decomposed by heating the mixture. The operation is terminated by the addition of peroxide of hydrogen to get all the manganese into solution, and washing the graphitic acid formed.—*Berichte*, vol. xxxii., p. 1394.

New Method for the Estimation of Glycogen.—Pflüger and Nerking.—If we dissolve meat by means of boiling caustic soda, we can separate, in the liquor obtained, the glycogen from the proteic substances by the following method:—To 100 c.c. of liquor containing 3 grms. of caustic soda or potash we add 10 grms. of iodide of potassium and 50 c.c. of alcohol at 96 per cent; the glycogen is entirely precipitated. If we separate the precipitate by filtration, and wash the precipitate on the filter with a solution prepared by mixing 50 c.c. of alcohol at 96 per cent with 100 c.c. of water containing 3 grms. of caustic potash and 10 grms. of iodide of potassium, and if, finally, we re-dissolve this washed precipitate in water, we find that this solution which contains all the glycogen of the original liquid does not contain any proteic materials. We thus have at our disposal a more simple and as exact a process as that of Brücke for separating the glycogen from proteic matters, a process which can be used with great advantage for the preparation and estimation of glycogen in extracts of tissues.—*Pflüger's Archiv*, vol. lxxvi., p. 531.

The Solubility of Copper in an Alkaline Solution of Gelatin.—A. Lidof.—The author has observed that the violet solution obtained by the reaction of salts of copper on an alkaline solution of gelatin is decomposed when heated under pressure in a Lintner apparatus, and that metallic copper is deposited. The same result is obtained in the cold ten or fifteen hours after formic aldehyde has been added. The precipitate, however, is not pure copper, but contains a certain amount of organic matter, and only 92 per cent of copper. From this the author is inclined to the opinion that the so-called biuret action is nothing else than the passage of copper into solution; that is to say that the salts of copper are reduced by the organic matter, and that the metal takes a soluble colloidal form. Acting on this opinion the author has made the following experiment:—A spiral of copper weighing 39.487 grms., quite free from oxide, was plunged

into a solution of 150 grms. of water, 13.6 grms. of gelatin, and 14 grms. of KOH. On the following day the liquid already had a violet tint, which, as time passed, became of a deeper hue. After forty-eight days the spiral had lost 1.301 grm., or 3.54 per cent of its weight.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 571.

The Action of Heat, Dilute Acids, and Alcohol on Albumin.—A. Panormof.—If we dialyse albumin with solutions of 0.05 per cent to 0.5 per cent of HCl, HBr, PO_4H_3 , $\text{P}_2\text{O}_7\text{H}_4$, and PO_3H , soluble compounds with these acids are formed, except with the last. The rotatory power of the albumin has increased, especially with the HCl, and it increases still more when heated to 100° ; but analysis always shows the same composition for albumin combined with acids. The variation of the rotatory power appears to be due to a polymerisation of the albumin. If we decompose the compound formed with the acid without heating it, we recover the original crystallisable albumin; if we heat it to 100° we get an amorphous body with different properties, but having the same composition. In any case the albumin has the empirical composition $\text{Alb} = \text{C}_{258}\text{H}_{422}\text{N}_{63}\text{O}_{83}\text{S}_3$. The compounds obtained by dialysis by the author and by M. Worms, are:—

	Per cent.
$\text{Alb}(\text{HCl})_5$ with HCl at	0.1
$\text{Alb}(\text{HBr})_3$ with HBr at	0.1
$\text{Alb}(\text{PO}_4\text{H}_3)_2$ with PO_4H_3 at	0.05
$\text{Alb}(\text{PO}_4\text{H}_3)_3$ with PO_4H_3 at	0.2
$\text{Alb}(\text{PO}_4\text{H}_3)_4$ with PO_4H_3 at	0.5
$\text{Alb}(\text{P}_2\text{O}_7\text{H}_4)_3$ with $\text{P}_2\text{O}_7\text{H}_4$ at	0.2
$2\text{Alb}(\text{P}_2\text{O}_7\text{H}_4)_7$ with $\text{P}_2\text{O}_7\text{H}_4$ at	0.5

If we heat $\text{Alb}(\text{P}_2\text{O}_7\text{H}_4)_3$ or $2\text{Alb}(\text{P}_2\text{O}_7\text{H}_4)_7$ with the acid solutions which have furnished these compounds we obtain $\text{Alb}(\text{PO}_4\text{H}_3)_3$ or $\text{Alb}(\text{PO}_4\text{H}_3)_5$. Albumin, dialysed with water and then filtered, does not lose its solubility by concentration in vacuo; it, however, ceases to be soluble when heated in sealed tubes, or when precipitated by a mixture of alcohol and ether. In these latter cases a polymerisation is probably produced. According to the author acids, heat, and alcohol easily polymerise albumin; it is this that proves the constancy of the composition and the variation of certain properties, such as the rotatory power and the solubility.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 556.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2120

THE SENSITIVENESS OF SILVER AND OF SOME OTHER METALS TO LIGHT.*

By Major-General J. WATERHOUSE, I.S.C.,
(late Assistant Surveyor-General of India).

(Concluded from p. 4).

Images Formed on Both Sides of Exposed Glass Plate.—

In connection with this action through glass, a curious result obtained on a plain glass plate may be mentioned. A piece of clean glass plate was exposed for a day and a half in October under the same aluminium screen, with another glass plate over it, so as to protect the surface from the air. It showed a clear breath image, but mercury vapour did not produce any image. Iron development, however, brought out part of the design very clearly, the silver depositing upon the unexposed parts, and giving an image darker and clearer than the ground. The image of the design appeared by breathing on both sides of the exposed glass plate, so that the action of light went through both plates.

Effect Produced on Varnished Silver Glass.—With the same object of ascertaining whether the images could be produced when the silver surface was protected from the air by varnish, a silvered glass plate was coated over one half with photographic negative varnish, and then exposed in the usual way, under the cut-out paper mask and mica screen, in October. After exposure for two days the image of the black paper mask, the cut-out initials, and edges of the mica screen were not reproduced so clearly as usual, though they appeared readily enough on the unvarnished half when breathed upon. The distinct heightening of the effect under the varnished part is apparently due to some chemical combination, probably oxidation, or the formation of an organic silver compound sensitive to light. When the varnish is removed the strong image remains, and there is a distinct change of colour in the exposed part of the silver surface, which takes a sort of yellowish olive-grey tint. Recent repetitions of the experiment with silvered glass, and with a plate of nearly pure silver, gave exactly the same results. It may be noted that with iodised silver plates the same varnish has been found to exercise a decidedly retarding effect on printed-out images.

Probable Cause of the Effects Described.—As regards the cause of the peculiar effects described, and the nature of the visible and invisible but developable images produced by the action of light upon plain silver surfaces, it is very difficult to give any definite opinion. It would seem that in this, as in most photographic processes, the first action of light is principally molecular, but if the exposure be prolonged and takes place in the air under ordinary conditions, there is a certain chemical decomposition of the surface of the plate, and the impressed image becomes distinctly visible.

Moser.—Moser was of opinion that the action of light does not necessarily consist in the separation of two chemically combined bodies, even in the Daguerreotype, in which process he maintained there is no separation of iodine from silver under the action of light. (We now know that the iodine evolved is absorbed by the underlying silver). He brought forward his experiments on pure surfaces of silver, where, he says, there can be no possibility of a chemical action to show that the effects of the Daguerreotype could be produced in quite a different way.

Waidele.—Waidele (*Pogg. Ann.*, 1843, vol. lix.), although he does not refer to Moser's observation of the direct action of light upon silver, and concerns himself more with the contact actions attributed to invisible light, concludes that Moser's effects are not produced by any action of invisible light, but must be rather explained by the action of atmospheres on bodies and the absorption of gases. He points out that polishing powders, such as tripoli, charcoal, &c., ordinarily contain moisture and absorbed gases, for which they have a strong attraction, and if used in this state they give up these vapours to the surface polished. If, however, they are heated to a red heat to drive off all moisture and gases, they then act as absorbents, drawing out the moisture and gaseous impurities from the surface of the metal, and producing a far purer and more perfect polish. He also notes the effect of carbonic acid, hydrogen, and other vapours on iodised silver Daguerreotype plates.

So far as my experiments go, I do not think that the nature of the polishing materials has had much influence on the results obtained, though it is an interesting point which might be looked into.

Roscoe.—Roscoe (*"Watts's Dict. of Chem."*, 1872, ii., p. 805) also attributes the Moser effects to absorbed gases, and says:—"Almost all of the singular phenomena first investigated by Moser, and ascribed by him to the action of latent light, may be more rationally explained by the authenticated facts of the absorption of gases by solid bodies." He also refers more particularly to the contact or "breath" images produced by laying coins, &c., upon polished plates of metal.

Action of Gases.—It is evident that if there be any chemical action on the silver under the influence of light, it must be produced by the agency of gases or vapours contained:—

- (i.). In the silver itself.
- (ii.). In the layer of air or condensed gases in immediate contact with the plate.
- (iii.). In the surrounding atmosphere.
- (iv.). In the masks or coverings under which the exposures are made.

What the exact nature of the decomposition may be, and to which of these agencies it is attributable, is not easy to ascertain, nor does the appearance of the visible image give much clue to it. From the dull-grey colour of the exposed parts it seems, however, probable that oxygen plays an important part in the action; but whether the oxygen is drawn from the air or is disengaged from the metal itself, or whether both actions takes place with interactions of other gases occluded in the metal itself or present in the atmosphere in contact with its surface, there is nothing so far to definitely show. It seems also probable that, as in many other photographic processes, the presence of watery vapour is necessary to bring about the decomposition. These points require further investigation at a time of the year when the light is bright, and the effects can be observed under the most favourable conditions. From the fact that in most of my experiments the external air has been excluded by the outer glasses of the printing frames, we may, I think, conclude that the effects are due more to the gases or vapours occluded in or attached to the silver surface or to the screens, rather than to any outside atmospheric influences.

Oxygen Found in Silver by Graham.—With regard to the presence of oxygen in silver, Graham found that silver heated and allowed to cool in oxygen could occlude 0.745 volume of oxygen, which was permanently fixed in the metal at all temperatures below an incipient red heat. It did not tarnish the bright metallic surface of the silver, or produce any appearance suggestive of the oxidation of a metal. He further showed that silver in the form of sponge can occlude eight volumes of oxygen without any visible tarnish. Silver appears to have a relation to oxygen similar to that exhibited by platinum, palladium, and iron to hydrogen. Silver can also occlude variable quantities

* A Paper read before the Royal Society, May 31, 1900.

of hydrogen, nitrogen, and carbonic acid (*Phil. Trans.*, 1866, p. 434).

Dumas's Observations.—According to Dumas (*Comptes Rendus*, 1878, vol. lxxvi., p. 69), 1 kilo. of pure silver, prepared by fusion with borax and nitre, was heated in a vacuum to a temperature not exceeding a dull red, about 500° or 600° C. The evolution of gas continued for about six hours, and it was received over mercury. The gas given off was pure oxygen, amounting to 47 c.c. at 0°, and 760 m.m. of pressure for 1 kilo. of silver, and weighing 82 milligrams. In two other experiments, in which silver was fused in a more oxygenated atmosphere, as much as 158 c.c. of oxygen, weighing 226 milligrams., and 174 c.c., weighing 249 milligrams., were obtained from 1 kilo. of pure silver in each case. He found also that silver which contains oxygen does not lose it all in a cold vacuum.

Mallet's Observations.—Professor J. W. Mallet, in some investigations on the Atomic Weight of Aluminium, notes these results obtained by Dumas, and states that in his own observations of the same kind, but using a lime support for the silver heated in a hard glass tube to a moderate redness, he obtained only 34.63 c.c. of oxygen from 1 kilo. of silver (*Phil. Trans.*, 1880, p. 1020).

These different observations show that silver, apparently pure, may contain a very considerable quantity of oxygen, and I believe it is a well-known fact, especially in the Mints, that oxygen is nearly always present in silver, with or without hydrogen, carbonic acid, and other gaseous impurities in much smaller quantities.

Whether occluded oxygen is the cause of the photographic effects produced on surfaces of apparently pure silver might readily be proved by extracting all the oxygen from a silver plate by the above methods, and then exposing the resulting purified silver to light, a similar plate from which the oxygen had not been extracted being exposed at the same time. I have not the appliances at my disposal for making this experiment.

Effects of Heating Silver Plates to Redness.—With regard, however, to the effect of simply heating the silver plates to redness, the following experiments may be of interest, and seem to show that the heating, whether accompanied by subsequent "blanching" or "pickling" in dilute sulphuric acid or not, causes a distinct loss of sensitiveness, and in some cases may destroy it entirely.

A piece of thin, pure silver plate was first of all heated to a red heat over a spirit-lamp, then plunged into dilute sulphuric acid, and, after being washed with distilled water and dried, was exposed for about two days and a half, partly in sunshine, at the end of September last, under a screen of mica carrying a cut-out design in tinfoil, which had also been passed through the flame of the lamp. No visible image was produced, nor did one appear by breathing on the plate. Development with acid ferrous sulphate and silver nitrate brought out traces of the opaque tinfoil mask, and of parts cut out of the mica. The free ends of the plate, which were exposed to the air all the time, did not show any distinct attraction for the developer.

Another plate of pure silver, well cleaned with "meteoric" polish (No. 2) and exposed as usual under a mica screen with black paper mask, only one day longer than the last plate, gave a very strong visible image requiring no development. There must, therefore, have been a considerable difference in the conditions of the surfaces of the two plates.

In the plate which was heated and then treated with dilute sulphuric acid, it may be assumed that any surface layer of condensed gases must have been destroyed, and a surface of pure metal exposed—which, as one would expect, was not visibly sensitive to light. In the other case, in which the plate was probably oxidised (it had been lying by for several years), and was simply well cleaned with a dry polishing powder, the surface of the metal was left so sensitive to light as to give a strong visible image. This difference of action in two plates, which were ex-

posed to the same conditions of light, seems to show that the effects produced by light on surfaces of metallic silver are chemical rather than merely molecular in their nature.

A repetition of this observation gave similar results. Further, a plate of thin silver foil, well heated over the spirit-lamp and exposed under a mica screen, which was also heated, for two days, including some hours of sunshine, showed no image, even on development with mercury, although distinctly visible images had been obtained on the same piece of foil when cleaned in the ordinary way and exposed under the same or similar screens. Further experiment on this point is still necessary.

Effects on Silver Surfaces Fumed with Acid and other Vapours.—A good many experiments have been made with silvered glass plates or silver foil, fumed with various vapours, which might possibly be present in small quantities during the exposure to light, among them hydrogen peroxide, nitric acid, ammonia, also sulphurous acid; these plates have all shown visible and developable images of a somewhat similar character to those formed on the plain metal.

Nitric Acid.—By fuming silvered glass plates with ordinary pure nitric acid (1.420) or, better, with the same acid diluted with an equal volume of water, very clear positive printed-out images have been obtained, even with the comparatively short exposure of one hour in the February sun. With a longer exposure the image was clearer, the exposed parts appearing lighter than the protected parts, as is also the case with the plain silver surfaces.

Dilute Ammonia.—Dilute ammonia containing one part of the solution at 0.880 in 30 of water gave a similar image, but the film was not so sensitive as with the nitric acid. Further experiments have, however, to be made.

Dilute Sulphurous Acid.—Dilute sulphurous acid, formed by acidifying a solution of sodium sulphite with sulphuric acid, gave a weak image of much the same character.

Hydrogen Peroxide Solution.—Silvered glass plates, fumed with various strengths of hydrogen peroxide solution, have given fairly sensitive films, sometimes a little white in appearance, but as a rule the printed-out images produced on exposure to light are just the reverse of those produced on plain plates and those fumed, as noted above, i.e., the parts exposed appear darker than the unexposed parts, and do not attract mercury vapour, so that a positive picture is produced from an ordinary black and white negative. By long exposure this effect is sometimes reversed. The visible images produced on silvered glass plates fumed with the peroxide quickly fade away, though the details may still remain visible on breathing. The same effect of fading out has also been observed on plain silver plates.

Rain or Boiled Distilled Water.—Silver plates exposed under fresh, clean rain water, or boiled distilled water, gave distinct images on development with mercury, but not very readily, and further observations are necessary.

Exposures in Fluid Hydrocarbons.—In order to ascertain whether the images would be produced on silver surfaces exposed in fluid hydrocarbons containing no oxygen, silvered glass and pure silver foil were exposed in fluid paraffin, benzole, xylol, and toluol.

Paraffin.—In clear, colourless, fluid paraffin very strong dark olive-yellow images were produced by light on silvered glass and silver foil on the parts exposed freely in the fluid or under the parts cut out of a black cardboard mask, but under a mica screen, which covered part of the black mask, and of the plate itself, there was no darkening action whatever. The darkening appears to be due to sulphuration, but why it should not occur under the mica is not clear, unless the latter cuts off the rays which are active in producing it.

Benzole.—Silver foil well cleaned and exposed in ordinary rectified benzole under a cut-out black paper mask, and also half covered with mica, showed very clear,

yellow images of the cut-out design on the part uncovered by the mica, apparently by decomposition of thiophene or other sulphur compound present in the benzole. This darkening required strong sunshine to produce it, and on prolonging the exposure in the sun the metal became quite bronzed in the uncovered exposed part, while the part protected by the mica also took a light tint. It may be noted that, as a rule, the backs of these slips of foil (which were exposed in test-tubes) were not protected by any covering, but showed no perceptible change of colour: the darkening of the exposed foil was therefore solely an effect of light.

Effect of Heating the Foil.—A piece of the same foil was exposed in the same way in the same benzole after being heated to redness. This did not show such a strong image, even by long exposure in the sun.

A piece of pure foil (assay foil) was exposed in a purer sample of benzole, and also gave a distinct yellow image as soon as the sun acted upon it after some days' exposure, the light being dull till near the end of the period. Another piece of the same foil, heated to redness and exposed at the same time, only showed a very pale yellowing.

Xylol.—A similar very faint, but browner, change of colour was noticed on a piece of the same foil, not heated, exposed for several days in commercial pure xylol.

With toluol, similar results were obtained after long exposure.

Effects of Light upon other Metals.—A few observations have been made as to the action of light upon other metals, but with the exception of lead none of them have proved very sensitive, and further work is necessary in good weather.

Gold.—Images developable with mercury have been obtained on gold leaf by prolonged exposures, but scarcely any trace of a developable image could be obtained on some highly-polished well-gilt buttons exposed for several days in good sunshine in October.

Lead Foil.—On pure lead foil I have obtained a very distinct darkened image visible after exposure. Very distinct darkening was also produced on lead foil exposed in pure benzole.

Copper.—On copper distinct visible images have been obtainable sometimes, but the metal is not so sensitive as silver to light, though I have readily obtained heat images on it developable by mercury. Pure copper foil exposed in sunshine in pure benzole showed a distinct darkening, but exposed in xylol it did not change colour.

Nickel, Platinum, Aluminium, Palladium.—Nickel, aluminium, and platinum appear to be quite insensitive to light, but with a small button of palladium, kindly lent to me by Mr. T. Bolas, which was exposed for some days under a black paper mask, there appeared a slight but fairly distinct trace of deposit of mercury on the exposed parts. The spot was too small to make sure of.

Trial with Röntgen Rays.—With the kind assistance of Mr. F. H. Glew I was able to make a few experiments with the Röntgen rays upon silvered glass and pure silver plates, exposed for several hours to the rays, but without any visible or developable effect.

The above is a summary of my observations in this direction so far as they have gone. I hoped to have made them more complete, but the dull winter weather has been very much against such work. I hope, however, to go on with it during the summer, but think it advisable to publish the results already obtained now, in order that others may be able to extend them at the same time. They show, I think, that most of the phenomena that occur by the exposure of ordinary photographic plates containing haloid compounds of silver can be observed upon a plain silver plate exposed to light in the air under ordinary conditions. It seems not impossible, therefore, that the key to the hitherto unsolved problem of the production and constitution of the so-called "latent photographic image" may be found within these limits.

THE EIGHTH GROUP OF THE PERIODIC SYSTEM AND SOME OF ITS PROBLEMS.*

By JAS. LEWIS HOWE.

In the early work of Newlands and of Mendeléeff, which subsequently developed into the periodic law, a serious difficulty was met with in dealing with iron, cobalt, nickel, and the metals of the platinum group. In Newlands' modified statement of his law of octaves he says: "The numbers of analogous elements, when not consecutive, differ by seven or by some multiple of seven." Thus we find him grouping (CHEM. NEWS, 1866, xlii., 130) cobalt and nickel under a single number; so rhodium and ruthenium; so also platinum and iridium. Cobalt, nickel, palladium, platinum, and iridium are considered by him analogous elements, each occupying the first place in the octave to which it belongs; iron, rhodium, ruthenium, and gold are analogous elements, each occupying the seventh place in its octave, while osmium is included with copper and silver as the second members of their octaves. There was here an easily recognised inconsistency which was not cleared up till many years later Seubert was led by the study of the periodic law to revise the atomic weights of these metals.

In his first summing up of the principles of the periodic law in 1869, Mendeléeff concludes that "elements which are similar, as regards their chemical properties, have atomic weights which are either of nearly the same value (e.g., platinum, iridium, osmium) or which increase regularly (e.g., potassium, rubidium, cesium)" (*Journ. Phys. Chem. Soc. Russ.*, 1869, i., 60). So in most schemes for representing the periodic system, each triplet of these elements is considered as a single element, and because even then they do not seem to fall into regular periodic arrangement they are cast out, Ishmael-like, into an anomalous eighth group. This is doubtless the reason they have been relatively so much neglected by chemists, and possibly it is not incorrect to say that the chemistry of these metals is less known than that of any other group of well characterised elements. Yet there are certainly no nine nearly-related elements which present so many interesting chemical problems, whose solutions will so much further our knowledge of chemistry in general. It is the purpose of this address to attract the attention of the members of this section to this group and some of its many problems.

The ordinary division of these nine metals is into three groups, viz., the common metals, iron, cobalt, and nickel, with an atomic weight of from 56 to 59, and a specific gravity of 7.8 to 8.9; the lighter platinum metals, ruthenium, rhodium, and palladium, with an atomic weight of 101.5 to 106.5, and a specific gravity of about 12; and the heavy platinum metals, osmium, iridium, and platinum, of atomic weight 191 to 195, and specific gravity 21.5 to 22.5.

Of these metals iron alone can be considered abundant, and was the only one known until the eighteenth century. The ores of cobalt and nickel have been known for over two centuries, but the probable presence of a new metal in cobalt ore was first pointed out by Brandt (*Akta Reg. Soc. Sci. Upsala*, 1735, 33) in 1735, and nineteen years later Cronstedt (*K. Svenska Vet. Akad. Handl.*, 1751, 293) determined the existence of nickel. Both of these discoveries were several decades after confirmed by Bergman (*Opusc.*, Diss 20, 1775; 1780, xxiv., 12 and 14; 1779, xxv., 31 and 33).

It is, however, a curious and interesting fact that a coin of Bactria (*Pogg. Ann. der Phys.*, 1870, cxxxix., 507) of a date more than two centuries before Christ has been found containing 20 per cent of nickel, and hence quite similar in composition to our modern "nickels." There

* An Address delivered before the American Association for the Advancement of Science, Section C.

seem, however, to be no references in ancient literature which would indicate that attention was ever attracted by nickel or any of its compounds.

Turning to the platinum metals, the first recognised mention of platinum seems to be in the "Relacion Historica" of Don Antonio de Ulloa (vol. i., lib. vi., cap. 10, p. 606), published first in 1748, the book being an account of the French expedition of 1735 to the western coast of

From the mention here made, platinum is evidently a well-known substance, and it is by no means improbable that earlier definite mention of platinum may yet be found. In this connection it is interesting to note that there have been many efforts to show that platinum was known at much earlier periods. Scherer (*Allg. Z. Chem.*, Scherer, 1801, vi., 633) considers, from a passage in Balbin's "History of Bohemia" (P. I., ch. xiv., p. 4), that platinum was

PERIODIC TABLE, BY F. P. VENABLE—MODIFIED.

H												He					
Li		Gl		B		C		N		O		F		Ne			
Na		Mg		Al		Si		P		S		Cl		Ar			
K	Cu	Ca	Zn	Sc	Ga	Ti	Ge	V	As	Cr	Se	Mn	Br	Fe	Co	Ni	
														?	?		
														[82]	[84]		
Rb	Ag	Sr	Cd	Y	In	Zr	Sn	Cb	Sb	Mo	Te	—	I	Ru	Rh	Pd	
Cs	†	Ba	†	La	†	Ce	†	*	†	*	†	*	†	*	*	*	
*	Au	*	Hg	*	Tl	Pb	Ta	Bi	W	*	†	*	†	Os	Ir	Pt	
*		*		*		Th	*		U								
+	-	+	-	+	-	+	-	+	-	+	-	+	-				
Series.		Series.															

* Possible + series elements.

† Possible — series elements.

— Ekamanganese.

South America to measure an arc of the meridian on the equator. The passage reads: In the district of Chocó (Columbia), which contains many placer mines, are also found some, the gold of which, occurring mixed with other substances as metals and rocks, or being enveloped in them, requires the use of quicksilver for its extraction, and sometimes ores are found which are not worked, because of the *platina* in them (a mineral of such resistance that it is not easy to break it, nor to crush it upon an anvil), for this substance is not affected by calcination, nor is there any means of extracting the metal which it contains, except at the cost of much labour and expense.

known to the Bohemian Jesuits toward the end of the seventeenth century, occurring in the Riesengebirge, for he speaks of a kind of gold so white that one would swear it was silver,* were it not for its weight, ductility, infusibility, and insolubility in nitric acid. Julius Scaliger's "Exercitationes Exotericæ de Subtilitate," published at Frankfort in 1601, makes mention of an infusible metal found in the mines of Mexico and Darien, which might

* Aurum album, quod argentum esse jures, nisi auro familiares proprietates aliud suaderent, pondus scilicet, extensibilitas, vis eludendi ignem et aquam fortem, solubilitas in aqua regia, &c.

seem to indicate platinum.* There have been, moreover, a number of efforts to show that platinum was known to antiquity under the names of *electrum* or of *plumbum candidum*. Cortinovis (*Opuscoli Scelti Sulla Scienze, &c.*, Milano, 1760) considers that the *electrum* of the ancients was platinum, and proves it to his own satisfaction from the Bible, from classic historians of nature and art, from poetry and from Homer.† A similar view is held by Schweigger (*J. Prakt. Chem.*, 1845, xxxiv., 385), where Pansanius (v., Chap. 12, p. 406, Ed. Casaub.) is quoted as mentioning *electrum*, from which Augustus had made columns, as occurring in nature in the sands of the river Eridanus, and as being very rare, hence much more valuable than the other kind of *electrum* which is merely an alloy of silver and gold. In 1850 Paravey (*Comptes Rendus*, 1850, xxxi., 179) makes a strong effort to show that Pliny, when speaking in his *Natural History of plumbum candidum*, refers to platinum. Pliny speaks, indeed, of a lead heavier and more ductile than gold, and in Book 34, Chapter 16, gives a definite description of it. To use the quaint translation of Philemon Holland, Doctor of Physicke, published first in 1607:—

"Now insueth the discourse of lead and the nature of it, of which there be two principall kinde, the blacke and the white. The richest of all, and that which carrieth the greatest price, is that which we in Latine name *plumbum candidum*, i.e., the white bright lead, and the Greeks *Cassiteron*. But I hold it a meere fable and vaine tale, that all of it is fetched as farre as from the Islands of the Atlantick Sea, and that the inhabitants of those parts doe conveigh it in little twiggen boats, couered all ouer with feathers. For the truth is that there is found of it in these daies within Portugall and Gallacia, growing ebbe upon the opmost face of the earth, being among the sands, of a black colour, and by the weight only is knowne from the rest of the soile: and here and there among, a man shall meet with small stones of the same stuffe, most of all within the brookes, that be dry sometimes of the yere. This sandie and grauely substance, the mine masters and mettall finers use to wash, and that which setteth downeward, they burne and melt in the furnace. There is found likewise in the gold mines a kind of lead ore which they cal *Elutia*; for that the water that they let into these mines (as I said before) washeth and carrieth down withall certain little blacke stones streaked and marked a little with a kind of white, and as heavy they be in hand as the very ore of gold; and therefore gathered they be with the same ore, and laid in the paniers together therewith; and afterward in the furnace when the fire hath made a separation between them and gold, so soone as they are melted do resoluë into the substance of the white lead or tin glance aforesaid."

If Pliny's observation that this variety of *plumbum candidum* is as heavy as gold could be relied upon, the view would be plausible that he was cognisant of platinum, but unfortunately in other places he gives evidence of great inaccuracy in this respect. So, too, there seems no good reason for considering the metallic *electrum* to be anything other than the natural or artificial white alloy of gold and silver. If there were any question as to whether platinum were known to the ancients, it would seem to be completely answered in the negative by the fact that no platinum object, no nugget, or grain of platinum has been found among ancient remains.

Soon after the introduction of platinum into Europe, no inconsiderable amount of work was done upon it by Watson, Scheffer, Lewis, Macquer, Marggraf, Bergman, Guyton de Morveau, and others. A few chemists, led by

Buffon (*Obs. Sur. Phys.*, Rozier, 1774, iii., 322), cast doubts upon its elementary character. Buffon, when reading his *History of Minerals* to the Dijon Academy, held that platinum was an alloy of gold and iron, because it was attracted by a magnet, and, said he, if platinum be a metal there must be a second substance in nature attracted by a magnet. Von Milly believed that mercury was also present in the alloy, but Blondeau (*Obs. Sur. Phys.*, Rozier, 1774, iv., 154), professor of mathematics at Brest, showed the great improbability that platinum was anything other than a simple metal.

The first suggestion of a practical use for platinum seems to have come from Lavoisier's (*Annales de Chim.*, 1790, v., 137) observation of its value for laboratory utensils. Many efforts were made in the last decade of the eighteenth century to fuse platinum, or to get it into workable form. The first recorded success in this direction was that of Janetty,* a Parisian artisan, who melted platinum by alloying it with arsenic. It was also alloyed with lead and with bismuth, and then cupelled. Before 1800 l'abbé Rochon (*Ann. der Phys.*, Gilbert, 1800, iv., 282) wrapped grains of platinum in platinum foil, heated to redness and then hammered into an ingot. Moussin-Poushkin (*Chem. Ann.*, Crell, 1799, ii., 359) amalgamated platinum sponge with mercury and ignited in a muffle. Another process is described (*Phil. Mag.*, 1805, xxi., 175) of wrapping ammonium chloroplatinate in platinum foil, igniting, and hammering. In 1800 Knight (*Phil. Mag.*, 1800, vi.) published his process, which, with some modifications, was generally adopted, and remained in use till the metal was fused in the flame of an oxyhydrogen blow-pipe by Deville and Debray, more than half a century later. Knight's process consisted in heating platinum sponge in a nearly cylindrical but slightly tapering clay mould, and compressing it by a few hammer blows while in the furnace. This gave a coherent platinum which could be readily worked into an ingot. It was just about the opening of the century that the discovery of platinum in the Ural Mountains occurred,† and the supply being thus very materially augmented, the use of platinum in the laboratory became established. At the same time the study of the metal, from a chemical standpoint, led to the discovery of several other metals in the platinum ores. No less than five of the distinguished chemists of that day were working on the ore, with the special aim of separating out other metals which they had reason to believe were present. Palladium was first obtained by Wollaston; Collet Descotils was the first to publish indications of what we now know to be iridium, and Fourcroy and Vauquelin at the same time had this metal in hand in an impure form. The real discoverer of iridium should be recognised in Smithson Tennant, who not only separated it in purity, but also, at almost the same time, found in the same residues the element osmium, which seems to have been wholly overlooked by the French chemists. This chapter was closed a few months later by Wollaston's discovery of rhodium.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. The special thanks of the members were returned to Dr. Ludwig Mond for his donation of £150 to the Fund for the Promotion of Experimental Research at Low Temperatures. Mr. G. Livesey was elected a member.

* *Chem. Ann.*, Crell, 1790, ii., 53. The name is also spelled Jeanty, Jeannetty, and Jannetty.

† Osann says (*Pogg. Ann. der Phys.*, 1827, xi., 311) that the first mention he can find of platinum in connection with the Ural Mts. is *Ann. de Chim.*, 1806, ix., 317, where Vauquelin speaks of a rumour that platinum has been discovered in Siberia. Osann could not trace the origin of this rumour.

* *Praeterea scito infunduribus, qui tractus est inter Mexicum et Darien, fodinas esse auricalchi, quod nullo igni, nullis hispanicis artibus, hac tenus liquecere potuit.*

† As an instance of the views of Cortinovis may be cited the lines:—

Atrio cinxit ebur, trabibus solidatur ahenis
Culmen et in celas surgunt electra columnas,

from Claudian's *Rape of Proserpina* (Book I., v., 164), where it is considered that *electrum* must mean platinum.

A BIBLIOGRAPHY OF STEEL WORKS
ANALYSIS.

PART III.

By HARRY BREARLEY.

(Continued from p. 7).

CARBON (*continued*).

II. MODES OF RELEASING THE CARBON.

334. WEYL (*C. N.*, v., 170).—The sample is made the + pole of a dilute HCl cell. C residue retains form of the sample. The process was previously suggested by Binks (*C. N.*, v., 252).
335. OSMOND and WERTH (*C. N.*, lvi., 35).—Re-heated steel attacked by Weyl's process leaves a C-Fe residue which is explosive or spontaneously combustible.
336. BLOUNT (*C. N.*, lvii., 28).—Place borings on Pt plate in Cu solution, and suspend Cu plate thereover. Pass current so that Cu is removed from borings nearly as quickly as it is deposited on the upper plate. Escape of hydrocarbons thus obviated.
337. JUTSUM (*C. N.*, xli., 17).—Solution in acid Cu solution leads to loss through evolution of hydrocarbons. Uses Weyl's process. Rubber to limit action to a portion of the rod. Filters through a straight tube plugged with muslin, sand, &c. KHO containing KNO_2 absorbs O, and unduly increases the result.
338. HARTLEY (*C. N.*, xvi., 157). The gas liberated in Weyl's process may be such as was occluded by the iron.
339. BOUSSINGAULT (*C. N.*, xvii., 267).—Powdered sample triturated with HgCl_2 , the HgCl_2 volatilised in a current of H, and dried residue weighed.
340. BOUSSINGAULT (*J. I. S. I.*, 1886, 822).—Above process fails if more than 2 per cent Cr is present. Burns directly in O for thirty hours, or separation of Fe with Cl. FeW and FeMn are decomposed by the latter method.
341. FRESSENIUS (*C. N.*, xxi., 167).—Volatilise Fe with Cl. The chlorine must be thoroughly dry. See also NAUMANN and MUDFORD (*J. C. S.*, lxxii., ii., 209).
342. FRESSENIUS and HINTZ (*C. N.*, lxi., 67).—Release the C from FeCr in a current of Cl, and burn with CrO_3 and H_2SO_4 . Graphite is determined on 10 grms. of the sample after digesting for weeks in oft renewed HCl.
343. WATTS (*C. N.*, xlv., 279).—Discusses various modes of releasing the C. Volatilises Fe with Cl in fifteen minutes; describes apparatus and precautions.
344. GINTL (*J. I. S. I.*, 1885, 589).—Chlorine should be passed over heated charcoal before being used to decompose the sample. When Fe is rich in manganese MnCl_2 envelopes the C residue, and necessitates the subsequent use of a Cl absorbent.
345. SCHUTZENBERGER and BOURGEOIS (*C. N.*, xxxi., 207).—White cast-iron decomposed with CuSO_4 and an acid solution of Fe_2Cl_6 . The dried residue is a hydrate of carbon.
346. HOGG (*C. N.*, lviii., 199).— Fe_2Cl_6 may be used to decompose the precipitated Cu, or initially with the heated copper solution. If used alone it causes loss of C. Silicious steels filter badly after standing.
347. ZABOUDSKY (*C. N.*, l., 57).—Triturated in a pasty mass of cuprasodium chloride. Cu dissolved with Fe_2Cl_6 . Results of the colour process not comparable if metals are of different origin.
348. LANGLEY (*C. N.*, lxii., 227).—International standards' work. Values from 1.02 to 1.15 per cent due to use of variously crystallised, acidified, &c., Cu solutions.
349. LANGLEY (*J. I. S. I.*, 1891, ii., 321).—Above results due to tarry matter (pyridine) in cuprammonium salts. Recommends cuprapotassium salts.
350. DROWN (*C. N.*, lxi., 5).—Acidified CuCl_2 promptly dissolves the iron and gives good results.
351. ARNOLD ("Steel Works Analysis," p. 29).—Has observed bubbles of gaseous hydrocarbons on using acid CuCl_2 (see 337).
352. DUDLEY and PEASE (*J. I. S. I.*, 1894, i., 609).—Decompose Fe with cuprapotassium chloride. Duplicates agree to 0.005 per cent.
353. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 520).—Dissolve in cuprapotassium chloride in an atmosphere of CO_2 at 90°C . The moist residue is burned in oxygen.
354. CARNOT and GOUTAL (*J. S. C. I.*, 1899, 521).—Blair's recommendation—dissolving in an HCl solution of cupro-potassium chloride—leads to loss at temperatures of 70° and over. Dissolving in faintly acid solutions at 95° in atmosphere of CO_2 rapid and reliable, except for Fe-Mn.
355. GALBRAITH (*C. N.*, xxxv., 151).—The iron of chromium steels refuses to replace copper in the solution. (This is certainly not the case with cupro-ammonium chloride.—H. B.).
356. FÖRSTER (*C. N.*, lxxii., 293).—Some kinds of wrought iron, and tungsten steels especially, evolve hydrocarbons on being dissolved in a quite neutral solution of cuprammonium chloride. Cuprammonium oxalate is suggested.
357. BRAND (*J. I. S. I.*, 1887, ii., 364).—On separating the C with neutral or basic cuprammonium chloride, hydrocarbons are evolved, and tungsten steels are hardly worse than other kinds. The loss is very serious in low-carbon steels.
358. BRAND (*J. C. S.*, lii., 866).—Decompose with HCl containing 24 per cent Br; destroy Br with ammonium oxalate. Use Ag spiral in combustion-tube to retain traces of Br.
359. MOISSAN (*J. C. S.*, lxx., ii., 339).—Carbon is liberated from Al with HgCl_2 , Hg volatilised in H, and residue burned in oxygen (see 339). GONTIERE (*J. S. C. I.*, 1896, 830) uses cuprammonium chloride and wet combustion for Al and alloys.
360. BLAIR (*C. N.*, lxiv., 66).—The HCl solution gives higher results than the neutral solution of cuprammonium chloride. Determines C by direct combustion and volatilising Fe in HCl. Cuprous chloride and anhydrous CuSO_4 , the most efficient purifiers of CO_2 . Repetition of Dudley's work (348).
361. GIRARD (*J. I. S. I.*, 1899, i., 464).—Uses the cuprammonium chloride process for estimating C in FeCr or FeSi, for which the chromo-sulphuric acid process is not satisfactory.
362. BREARLEY (*C. N.*, lxxiv., 63).—The dissolving sample is kept stirred by attaching the containing flasks, fitted with tubes, to the filter-pump. Vigorous shaking in a closed flask prepares a sample for wet combustion in fifteen minutes.
363. J. T. (*C. N.*, lxxix., 169).—Accessory to above stirrer. Examination of the decomposition of steels with cuprammonium chloride and continued re-use of the same liquor.
364. RECKLINGHAUSEN (*J. C. S.*, lxxii., ii., 19).—A shaking apparatus, driven by a small motor.
365. DUNSTAN and DYMOND (*C. N.*, lxxv., 148).—A simple shaker, also driven by a motor.
366. WDOVISZEWSKI (*J. I. S. I.*, 1898, ii., 555).—Dissolves the sample of steel in cuprammonium chloride with a shaking apparatus in five to eight minutes.
367. ZABOUDSKY (*J. I. S. I.*, 1882, 357).—After treating white pig-iron with CuCl_2 the residue is $\text{C}_{12}\text{H}_6\text{O}_3$. It can be easily nitrated.
368. ZABOUDSKY (*J. I. S. I.*, 1884, 297).—Liberated with CuSO_4 and NaCl; the dried residue contains

- varying percentages of C, according to the nature of the sample. Extremes, 65.5 to 71 per cent.
369. DONATH (*J. I. S. I.*, 1898, i., 493).—Examination of the C. residue. Nitro-derivative prepared therefrom identical with the substance giving Eggertz colour. All the combined carbon is not evolved on dissolving in dilute acid.
370. JUPTNER (*J. I. S. I.*, 1896, ii., 422). *Resumé* of the examinations made of the carbonaceous residue, gases liberated on dissolving steel and the state in which C exists in steel.
371. BÄCKSTRÖM and PAJJKULL (*J. C. S.*, liv., 420).—Volume and character of gases evolved on decomposing steel with acids; liquid hydrocarbons formed.
(To be continued).

COLORIMETRIC ESTIMATION OF VANADIUM.

By L. MAILLARD,

DURING the course of a series of physiological experiments, I was led to search for a simple, rapid, and convenient method for the estimation of small quantities of vanadium in the form of vanadic acid, or of an alkaline vanadate. These quantities being, as a rule milligrams only, and rarely amounting to as much as a centigram, mixed with large quantities of other salts, the ordinary gravimetric methods were not to be trusted. The same may be said of the volumetric methods based on the reduction of permanganate.

In chemico-physiological or toxicological researches it is of advantage to reduce manipulation to a minimum, and to effect the estimation of particular bodies without first attempting too high a purification, on account of the inevitable losses which render the relative error too high when working on such small quantities. The estimation must also be founded on a specific reaction, and not a common-place one, such as the reduction of permanganate, which might be influenced by the presence of all kinds of impurities.

I have utilised the well-known reaction of peroxide of hydrogen on vanadic acid described by Barreswill ("Note on a New Oxygenated Compound of Chromium," *Ann. Chim. Phys.*, 1847, Series 3, xx., p. 364), in the year 1847, and attributed by him to the formation of a pervanadic acid analogous to perchromic acid which he had just discovered. Peroxide of hydrogen, ether saturated with peroxide of hydrogen, ozonised ether, and ozonised essence of turpentine, when placed in contact with a strongly acid solution of a vanadate, develop a magnificent red colouration, which is still noticeable in a solution of 1/84,000th, as has been shown by G. Werther (*Fourn. f. Prakt. Ch.*, 1861, vol. lxxviii., p. 195). This reaction is commonly used for detecting the presence of vanadic acid, but up to the present no author, to my knowledge at least, has proposed to use it for a colorimetric estimation. I therefore decided to find out whether the formation of pervanadic acid was total, and if the depth of colour could be made to serve as an exact measurement of the proportion of vanadium in the solution.

I first prepared a mother-liquor of metavanadate of sodium at one-tenth by means of the pure salt; I then made dilute solutions of metavanadate of 1/100th and 1/1000th, which served as standards of comparison. With the same solution of one-tenth I prepared dilute solutions containing various quantities of metavanadate, quantities which were actually known, but which I treated as unknown, and which I estimated by means of Duboscq's colorimeter by comparing them with the 1/1000th solution. The results always gave perfect concordance.

Into a graduated test-jar, very narrow and very tall, containing 25 c.c., I poured 20 c.c. of the neutral solution under examination. I then added, according to the quantity of vanadate, from 1 to 5 c.c. of pure hydrochloric

acid; then from 3 to 10 c.c. of ether saturated with peroxide of hydrogen, H_2O_2 . This ethereal solution is prepared in advance by leaving equal volumes of ordinary ether and commercial peroxide of hydrogen at ten volumes alone together in a flask. The acidity of this peroxide of hydrogen is of no account, since the operation must be carried out in a very acid solution. I then corked up the test-jar and shook it up well; immediately the aqueous liquid takes a more or less intense red colour, and the supernatant ether remains perfectly colourless. I then poured a little distilled water into the test-jar to bring the volume of the aqueous portion up to 15 c.c.

If we carry out the same operation on the titrated solution of metavanadate at 1/1000th, it suffices to place the two red liquids in the cells of the colorimeter, and to vary the thicknesses until the tints are equal. The amount of vanadium is inversely proportional to the thickness. To test this method of working, I made a large number of verifications bearing on the following points:—

1. The intensity of the colouration produced in a solution of metavanadate at 1/1000th is always the same. For example, three experiments were made with the following proportions of reagents:—

- A. 10 c.c. of metavanadate at 1/1000th + 2 c.c. of ether H_2O_2 + 0.5 c.c. of HCl.
- B. 10 c.c. of metavanadate at 1/1000th + 3 c.c. of ether H_2O_2 + 2 c.c. of HCl.
- C. 10 c.c. of metavanadate at 1/1000th + 4 c.c. of ether H_2O_2 + 1 c.c. of HCl.

These gave colours exactly identical.

2. The intensity of the colouration produced in a solution at 1/100th is exactly ten times greater than in solutions at 1/1000th; this is proved by numerous experiments. It is of great importance to use sufficient quantities of the reagents. I varied the volumes of ether and of HCl used for estimating a solution at 1/100th, of which the concentration x was assumed to be unknown, the solution at 1/1000th representing unity. I always took 10 c.c. of metavanadate at 1/100th, and obtained the following values for x :—

Metavanadate at 1/100th. C.c.	Ether saturated with H_2O_2 . C.c.	HCl.	x .
10	2	1	5.56
10	4	1	6.12
10	6	3.5	8.43
10	10	4	10.00

We thus see that to obtain a complete reaction it is necessary to take for 10 c.c. of metavanadate at 1/100th, 10 c.c. of ether saturated with H_2O_2 , and 4 c.c. of HCl. For 10 c.c. of metavanadate at 1/1000th, 2 c.c. of ether, and $\frac{1}{2}$ or 1 c.c. of HCl would be sufficient. The necessary amounts of reagents in any particular case can therefore be judged according to the supposed concentration, or by means of a preliminary experiment.

3. The coloured solution can be diluted at will without undergoing any variation in the total amount of colouring matter; we can thus always bring the tint to be estimated into the neighbourhood of the standard tint. This is of great importance for ensuring accuracy of estimation, which is the more sensitive as the tints to be compared are closer and more dilute. In this manner a solution at 1/100th treated as above, then diluted to 150 c.c. (that is the aqueous portion), gives, by comparison with the solution at 1/1000th taken as unity, the following results:—

Thickness in m.m. of the standard solution.	Thickness in m.m. of the solution diluted to $x/10$.	$x/10$.	x .
5.0	5.0	1.0	10.0
10.0	10.0	1.0	10.0
15.0	15.1	0.9933	9.933
20.0	19.95	1.0025	10.025

The accuracy of the estimation has no other limit than the sensibility of the eye to the red rays.

4. The colouration remains for hours, and even days, when sufficient ether is employed; the measurements may therefore be made without any undue hurry.

5. Finally, the colouration should not be influenced by impurities in the solution. I have not experimented with the salts of the heavy metals, which are easily got rid of, inasmuch as H_2S does not precipitate the vanadates, and that the precipitate formed by $(NH_4)_2S$ is soluble in excess of this reagent. But in toxicological research we may come across salts, such as nitre produced by calcinations, chlorides of potash and ammonia introduced by neutralisations, sulphates and phosphates coming from the phosphorus and sulphur of the tissues, and, finally, the alkaline-earthly salts. I therefore prepared a series of solutions containing all of these. In 100 c.c. I placed 0.1 grm. of metavanadate of sodium $NaVO_3$, plus 5 grms. (that is to say fifty times as much), of each of the following salts:— KCl , NH_4Cl , K_2SO_4 , KNO_3 , Na_2HPO_4 , and $CaCl_2$. The colorimetric method did not show any difference between these various solutions and pure metavanadate, at 1/1000th.

This method will thus be of great use, as much through its accuracy as its rapidity. A standard of comparison is necessary, which may be either a solution of vanadic acid or a vanadate, carefully titrated once for all by the ordinary method. In practice it will be found to be advantageous to replace it by a suitably tinted red glass. This should not be too deep in colour, or the sensitiveness will be diminished. The most suitable tint seems to me to be that possessed by a solution of metavanadate at 1/1000th, viewed through a thickness of about 15 m.m. A similar sheet of glass, previously accurately standardised, will dispense with the necessity for operating with the standard solution on every occasion; it will also reduce the manipulation to one-half, and will enable a complete estimation to be made in less than five minutes.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 12.

THE ESTIMATION OF SUCCINIC ACID IN FERMENTED LIQUIDS.

By J. LABORDE and L. MOREAU.

THE methods now in use (Pasteur's method and Macagno's method) necessitate a great deal of manipulation and slow evaporations at the ordinary temperature, as there would be a loss of succinic acid at a higher temperature. This loss is due to a partial etherification of the acid by the glycerin contained in the liquors of fermentation. The author proposes the following method, which is quicker and quite as accurate as those already in use.

If we have to deal with liquors completely or nearly fermented, that is to say, not containing more than 1 per cent of sugar, we proceed as follows:—100 c.c. of the liquor are evaporated to dryness on the water-bath in a porcelain crucible having a flat bottom, together with 20 grms. of white sand previously washed with hydrochloric acid and calcined; the sand is well mixed with the residue, while the latter is still in a syrupy condition. The mass becomes hard on cooling. To facilitate its subsequent treatment, it is advisable to allow the mass to soften a little by exposing it to the action of the air for a few hours. It is then placed in a 250 c.c. matras, 100 grms. of No. 4 shot and 30 c.c. of ether are added. Agitation with the shot completely exhausts the mass after three fresh additions of ether, which is decanted each time on a flat filter. The ether is driven off, and the residue dissolved in a small quantity of boiling water, and a decimal solution of potash added in the presence of phenolphthalein. When the titration is finished an excess of potash is added, and we proceed to the saponification of the glyceric ethers; it suffices to evaporate the solution to dryness in a beaker on the water-bath, and to take up this

residue with water and titrate the free potash contained. The figure thus obtained for the total succinic acid is a little high; the error is due to a little volatile acidity, which is not completely driven off during the evaporation of the wine. To detect this volatile acidity it suffices to take up the liquor saturated with potash, to set free the volatile acid by tartaric acid, and to estimate it by distillation.

If we have to deal with incompletely fermented liquors, containing more than 1 per cent of sugar, we proceed as follows, remembering that too great a proportion of sugar interferes with the complete extraction of the succinic acid by the ether. The liquid is evaporated to a syrupy consistence, from 10 to 20 c.c. of alcohol are added, and some lead shot; we then introduce 50 c.c. of ether into the matras by small fractions, and thoroughly shake up the shot so as to cause intimate contact between the ether and the syrupy liquid, which is precipitated in the form of an emulsion. The ether is then decanted, a small quantity of alcohol is added, and the treatment with ether repeated. After three or four washings of this kind the whole of the succinic acid is removed. The ether is driven off by evaporation, and the alcoholic residue, placed in a flat-bottomed crucible with sand, is treated in the same manner as a liquor not containing any sugar.—*Ann. de l'Inst. Pasteur*, vol. xiii., p. 657.

ON THE AMMONIO-EARTHY PHOSPHATES.

By L. BARTHE.

IN certain treatises, particularly that of Kippenberger ("Grundlagen für den Nachweis von Giftstoffen," 1897, p. 222), we may find the formation of ammonio-barytic phosphate given according to the following equation:— $BaCl_2 + Na_2HPO_4 + NH_4OH = BaNH_4PO_4 + 2NaCl + H_2O$.

Taking the preparation of $BaNH_4PO_4$ for granted, we thought, without ever having seen it doubted, that the preparation of the ammonio-strontic phosphate would not offer any difficulties, and as we described the best conditions for the preparation of the different phosphates a few years ago (*Comptes Rendus*, 1892, vol. cxiv., p. 1267), it appeared to be of interest to prepare the amino-strontic phosphates of the general formula $(PO_4)_2Sr_2Am_2$, or PO_4SrAm , or again $(PO_4)_2SrAm_4$.

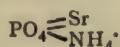
We therefore acted successively with methylamine, ethylamine, aniline, and β -toluidine on chloride of strontium mixed with disodic phosphate, these bodies being used in equimolecular proportions. Under these conditions the white precipitate obtained, when washed, does not contain any sensible proportion of nitrogen, and corresponds to the formation of bistrontic phosphate $(PO_3)_2Sr_2H_2$.

	I. Grms.	II. Grms.	Theory for $(PO_4)_2Sr_2H_2 = 367$.
Dried material ..	0.50	0.50	—
P_2O_5	37.50	37.50	—
P per cent ..	16.38	16.38	16.89
$SrSO_4$	0.505	0.5048	—
Sr per cent ..	48.13	48.12	47.68

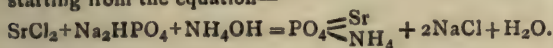
If we replace the amine by the hydrochlorate, and if to the mixture of the hydrochlorate of amine and chloride of strontium in concentrated aqueous solution we add disodic phosphate, we obtain a precipitate composed of phosphate of amine and phosphate of strontium. If we boil this mixed precipitate in several portions with distilled water, or if this same precipitate collected on a filter is thoroughly washed with cold alcohol, we obtain an amorphous, white, granular product hardly containing any nitrogen, and answering to the composition of the tristrontic phosphate, $(PO_4)_2Sr_3$.

	I. Grms.	II. Grms.	Theory for (PO ₄) ₂ Sr ₃ =452.5.
Dried material ..	0.50	0.50	—
P ₂ O ₅	32.00	31.00	—
P per cent ..	13.97	13.54	13.70
SrSO ₄	0.624	0.6249	—
Sr per cent ..	59.49	59.58	58.01

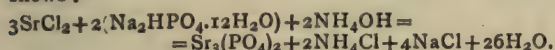
In the face of these results we may well doubt the existence of—



We therefore attempted to prepare this compound, starting from the equation—

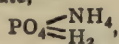


Whatever method of mixing these compounds was adopted, or whatever concentration of solutions was used, we always obtained a white, colloidal precipitate, answering to the formula (PO₄)₂Sr₃. The tristrontic phosphate is really formed as the following equation shows:—



We have already obtained (*Comptes Rendus, loc. cit.*) this same tristrontic phosphate by pouring a cold ammoniacal solution of 90 grms. of disodic phosphate crystals into a solution of 100 grms. of crystallised chloride of strontium; both these solutions should be quite free from carbonates.

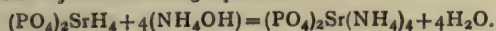
The preparation of the ammonio-strontic phosphate does not appear to have been effected by double decomposition. We have attempted to saturate a solution of monoammonic phosphate,—



which had been prepared by means of a saturated aqueous solution of strontia.

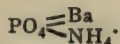
The addition of this latter solution immediately caused the appearance of a whitish magma, of which the chemical composition is very closely allied to that of the bistrontic phosphate.

Finally we have prepared the crystallised monostrontic phosphate. This compound was dissolved in a suitable quantity of water so as to facilitate its dissociation; ammonia was added in equimolecular proportion, as shown by the following equation:—



Immediately on the addition of the first drops of the alkaline solution a white precipitate is formed, which answers to the composition (PO₄)₂Sr₂H₄. No matter in what manner we have proceeded, we have been unable to obtain the ammoniostrontic phosphate.

There remained to verify the existence of the ammonio-barytic phosphate—



We have endeavoured to prepare this substance by taking advantage of the data furnished by the equation given by Kippenberger. As might be expected from the preceding results, we obtained bibarytic phosphate, (PO₄)₂Ba₂H₂.

	Grms.	Theory for (PO ₄) ₂ Ba ₂ H ₂ =466.
Dried material ..	0.5	—
BaSO ₄	0.502	—
Ba	0.2952	—
Ba per cent ..	59.04	58.80
P ₂ O ₅	28.0	—
P per cent ..	12.22	13.30

To sum up, with the exception of the ammonio-magnesian phosphate, NH₄MgPO₄, the other ammonio-earthly phosphates do not exist.

To estimate the alkaline-earthly metal in phosphates, it is best to dissolve, at a boiling temperature, 0.50 gm. of the dried, pulverised phosphate in 5 c.c. of normal hydrochloric acid and 20 c.c. of distilled water. To this solution we add a few cubic centimetres of sulphuric acid diluted to one-fifth. This is kept at the boiling-point for a few moments; after cooling we add 20 c.c. of strong alcohol. Filter, after a few hours, and wash thoroughly with dilute alcohol. However long the washing may last, we generally find that there remains on the filter with the earthy sulphate a small quantity of phosphoric acid, which may be detected by means of molybdate of ammonia.

As for the estimation of the phosphoric acid, this can be done volumetrically by means of uranium in the washwaters, without the necessity of converting it into the ammonio-magnesian phosphate precipitate, after having taken the precaution of driving off the greater part of the alcohol by evaporation.—*Bull. Soc. Chim.*, Series 3, vol. xxiii, No. 11.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 21st, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

A BALLOT for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. James Ashton; George E. Battle, B.A.; Charles Berjen Brooke, jun.; Angelo Cantin; Ernest Owen Courtman; Richard H. C. Gompertz, B.Sc.; John Henry Gough; Henry Bertie Gritton; Percy John Hinks; Tajiro Ichioka; John B. Leathes, M.A., M.B.; Alexander Ernest McKenzie; Hugh McNair; Sidney Scrivener Napper; David Herbert Patrick; M. C. Nanjunda Row, B.A., M.B.; M. Goolab Roy; Oswald Silberrad, Ph.D.; Timothy A. Smiddy; Herbert Procter Smith; George Edward Tomlins; John Traquair.

Of the following papers, those marked * were read:—

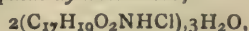
*89. "Researches on Morphine." I. By S. B. SCHRYVER and F. H. LEES.

The authors have found that the alcoholic hydroxyl group in morphine is readily replaceable, and they have prepared the compounds described below.

Chloromorphide, C₁₇H₁₈O₂NCl, prepared by the action of phosphorus trichloride on dry morphine. It melts at 190° with decomposition, and dissolves readily in chloroform and in methyl alcohol. The *hydrochloride*, C₁₇H₁₈O₂NCl.HCl, and *hydrobromide*, C₁₇H₁₈O₂NCl.HBr, have also been prepared. On treatment with acetic anhydride, the *monoacetyl* derivative, C₁₇H₁₇O(OC₂H₃O)NCl, is obtained, melting at 178–179°.

Bromomorphide, C₁₇H₁₈O₂NBr, melting with decomposition at 170°, has a very bitter taste and dissolves readily in chloroform and benzene. Its *hydrochloride* and *hydrobromide* crystallise with 1 molecule of water. Bromomorphide can also be prepared by the action of concentrated hydrobromic acid on morphine.

By treating chloromorphide with tin and hydrochloric acid, *desoxymorphine hydrochloride*,—



is obtained as glistening needles. The salt is lævotatory; [α]_D²⁷ = −140.3°.

It was found that on heating chloro- and bromomorphide and their hydrochlorides with water, decomposition took place, bromomorphide giving the hydrobromide of a base isomeric with morphine; for this new base the authors propose the name *isomorphine*. Isomorphine and its derivatives are more powerfully lævotatory than morphine and its corresponding deriva-

tives. The salts of isomorphine are much more readily soluble than those of morphine. Isomorphine melts at $246-247^{\circ}$, is readily soluble in methyl alcohol, but only very sparingly so in ether, chloroform, or benzene. Recrystallised from hot water, it is obtained as glistening needles. In methyl alcohol $[\alpha]_{D25} = -164.3^{\circ}$. For the hydrochloride, $C_{17}H_{19}O_3N \cdot HCl$ $[\alpha]_{D25} = -150^{\circ}$; for the hydrobromide, $C_{17}H_{19}O_3N \cdot HBr$, H_2O , $[\alpha]_{D20} = -127.2^{\circ}$ for the anhydrous salt. The methiodide, $C_{17}H_{19}O_3N \cdot CHI$, melts with vigorous decomposition at 279° ; in aqueous solution, $[\alpha]_{D25} = -91.5^{\circ}$. Morphine methiodide also melts at 279° , but for it $[\alpha]_D = -72.9^{\circ}$.

By treatment of isomorphine methiodide in aqueous solution with silver sulphate and barium hydroxide, a very alkaline solution of the hydroxide is obtained, which, dried in a vacuum, sets first to a deliquescent mass of fern-like crystals, and on further dehydration in a vacuum yields a solid which can readily be powdered. This substance dissolved in methyl alcohol does not react in the cold with methyl iodide, but does so readily on warming, giving a methiodide extremely soluble in water and in methyl alcohol, but only slightly so in ethyl alcohol. For it $[\alpha]_{D25} = 96.4^{\circ}$. This compound is not identical with codeine methiodide.

The determinations recorded in the following table were made with the free bases dissolved in methyl alcohol, and the salts (anhydrous) in water:—

Free base.	Hydrochloride.	Hydrobromide.
Morphine:		
$[\alpha]_{D23} = -130.9^{\circ}$	$[\alpha]_{D26} = -111.5^{\circ}$	$[\alpha]_{D20} = -100.4^{\circ}$
Chloromorphine:		
$[\alpha]_{D27} = -375.2$	$[\alpha]_{D21} = -313.7$	$[\alpha]_{D19} = -268.6$
Bromomorphine:		
$[\alpha]_{D25} = -65.6$	$[\alpha]_{D27} = +41.1$	$[\alpha]_{D25} = +39.5$

Chloromorphine, bromomorphine, desoxymorphine, and isomorphine are all devoid of narcotic action. The significance of these facts and the relationship between morphine and isomorphine were also discussed.

*90. "On the Oxime of Mesoxamide and some Allied Compounds." By MARTHA ANNIE WHITELEY, B.Sc.

The compound formed by the action of nitrosyl chloride on malonamide (Tilden and Forster, *Trans.*, 1895, lxxvii., 490) appears to be the isonitroso-derivative, $NH_2OC \cdot C(NOH) \cdot CONH_2$. It dissolves readily in water, has an acid reaction, and melts with decomposition at 187° . It forms alkaline salts which are bright yellow in colour and are easily soluble in water. Its most characteristic reaction is the production of an intense purple colouration when neutralised with an alkali and a solution of ferrous sulphate added: this is due to the formation of a double potassium ferrous salt, $KFe(C_3H_4N_3O_3)_3$, which crystallises from concentrated solutions in minute prisms having the lustre of bronze. The acetyl derivative of the oxime resembles the original substance in appearance, and melts with decomposition at 190° . The ethyl ether is crystalline, and melts at $150-151^{\circ}$.

The oxime can be prepared by the action of nitrous acid on the aqueous solution of malonamide, and by the action of hydroxylamine on dibromomalonamide.

By the action of nitrous acid on the oxime, a crystalline, sparingly soluble compound is obtained, which melts with decomposition at about 215° . It contains the proportion of nitrogen corresponding to a pseudo-nitrol of the formula $CONH_2 \cdot C \begin{smallmatrix} NO \\ NO_2 \end{smallmatrix} \cdot CONH_2$. It does not

respond to Lieberman's test, nor does it react as an oxime. By the continued action of nitrous acid, oxalic acid was the only solid product obtained.

The oxime is reduced by hydriodic acid to aminomalonamide, $CONH_2 \cdot CHNH_2 \cdot CONH_2$, the hydriodic acid of which crystallises in prisms.

The oxime of pyruvamide, $CH_3 \cdot C(NOH) \cdot CONH_2$, prepared by the action of ammonia on the oxime of ethyl pyruvate, melts at $176-177^{\circ}$, and closely resembles the

oxime of mesoxamide, but the alkaline solutions exhibit no decided yellow colour, whilst the colour produced by the addition of ferrous sulphate to the alkaline solution is reddish-brown. In attempting to prepare the oxime of pyruvamide by the joint action of ammonia and hydroxylamine on ethyl pyruvate, the chief product obtained was the oximidohydroxamic acid, $CH_3 \cdot C : NOH \cdot C \begin{smallmatrix} NOH \\ OH \end{smallmatrix}$, which is readily soluble, melts with decomposition at 143° , and is distinguished, not only by the cherry-red colour which is produced by the addition of ferric chloride, but by the production of an intense reddish-brown liquid and subsequent precipitate on the addition of ferrous sulphate to the alkaline solution.

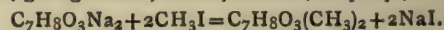
Succinamide submitted to the action of nitrosyl chloride or of nitrous acid is attacked but slowly, yielding succinic acid, but no oxime or other derivative.

Attempts to prepare Piutti's 8-oxime of the half acid ethyl succinic ester were not successful; this was apparently due to the spontaneous conversion of the β -compound into Ebert's α -isomeride. Cramer (*Ber.*, 1891, xxiv., 1204) represents the β -compound as the stable, and the α - as the labile isomeride.

*91. "On Dimethyldiacetylacetone, Tetramethylpyrone, and Orcinol Derivatives from Diacetylacetone." By J. N. COLLIE, F.R.S., and B. D. STEELE, M.Sc.

That dimethylpyrone is capable of acting as a basic substance, forming salts with acids, has already been clearly shown (Collie, *Trans.*, 1899, lxxv., 710). This work has been continued, and the basic properties of tetramethylpyrone have been investigated.

The sodium salt of dimethylpyrone reacts with methyl iodide, giving dimethyldiacetylacetone, m. p. 87° .—



When warmed with hydrochloric acid this compound loses water and is converted into tetramethylpyrone, $C_7H_8O_3(CH_3)_2 = C_7H_6O_2(CH_3)_2 + H_2O$. Tetramethylpyrone melts at 92° . It crystallises from water as a monohydrate, m. p. $63-64^{\circ}$: it forms a hydrochloride and a platinichloride, but appears to be less basic than dimethylpyrone. From the residues after separation of the dimethyldiacetylacetone, two other substances have been isolated:—(1) trimethylpyrone, $C_8H_{10}O_2$, m. p. 78° , which forms a platinichloride; and (2) a derivative of orcinol, $C_9H_{12}O_2$, m. p. 150° , possibly trimethyl-1:2:4-dihydroxy-3:5 benzene.

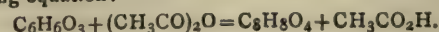
This orcinol derivative resembles mesorcinol in a very remarkable manner, but it is difficult to see how mesorcinol, which is 1:3:5-trimethyl-2:4-dihydroxybenzene, could be produced from dimethyldiacetylacetone.

A second orcinol derivative, $C_9H_{12}O_2$, was obtained by treating the crude product of the action of methyl iodide on disodiumdiacetylacetone with hydrochloric acid. It melts at 105° , and in all its reactions resembles the compound melting at 150° .

Dimethylpyrone unites with sodium ethoxide to form a compound, $C_7H_8O_2NaOEt$, which on treatment with acids yields ethyldiacetylacetone, $C_7H_9O_2Et$. This latter substance is very unstable, and easily decomposes into alcohol and dimethylpyrone when heated with acids.

*92. "Dehydracetic Acid." By J. N. COLLIE, F.R.S.

Since the publication of a paper on dehydracetic acid (Collie and Le Sueur, *Trans.*, 1894, lxx., 254), several reactions and the properties of various compounds of the acid have been investigated, all of which agree with the formula put forward by the author some years ago, namely, that dehydracetic acid is the lactone of tetracetic acid. The production of dehydracetic acid from triacetic lactone has been accomplished, as indicated by the following equation:—



Although neither acetyl chloride nor acetic anhydride react with triacetic lactone alone, if the lactone be boiled

with acetic anhydride and a little sulphuric acid or sodium acetate, dehydracetic acid is formed. The action of ammonia on the isomeric acid $C_6H_8O_4$ (obtained by Feist from the dichloride of dehydracetic acid) has been investigated, and an acid, $C_6H_9NO_3$, has been obtained identical with that previously isolated from the products of the action of heat on ethyl β -amidocrotonate.

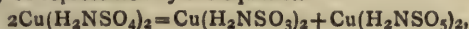
The production of dehydracetic acid from several of its dried salts has been studied. The dried sodium and silver salts treated with hydrogen chloride, and the dried lead salt with hydrogen sulphide, give dehydracetic acid.

The conductivity of a very pure sample of dehydracetic acid has been determined by Prof. J. Walker, who finds it to be 0.0001.

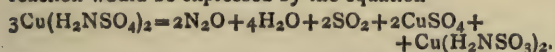
*93. "The Decomposition of Hydroxyamidosulphates by Copper Sulphate." By E. DIVERS and T. HAGA.

When a hydroxyamidosulphate is heated in solution with copper sulphate it is entirely decomposed. This takes place in such a manner as to throw much light on the nature of the obscure decompositions of these salts, as well as of the hydroximido sulphates and hydroxylamine salts when impure. No change is observed in the copper sulphate during the change it brings about, but of its alternate reduction and oxidation evidence is given, if, instead of the sulphate, cupric chloride be employed, as this is reduced to cuprous chloride.

The principal change caused by the copper sulphate may be represented by the equation—



the latter salt being represented by the actual products $Cu(H_2NSO_5)_2 = N_2O + H_2O + H_2SO_4 + CuSO_4$. Another change always takes place at the same time, being less marked when the temperature is low, and more so when the temperature is high. For example, a hydroximido-sulphate resists the action of the copper sulphate until the temperature of the solution is over 100° , when it hydrolyses to hydroxyamidosulphate, 28 per cent of which decomposes so that all its sulphur becomes dioxide, its hydrogen water, and its nitrogen nitrous oxide. If one-third of the hydroxyamidosulphate decomposed thus, the reaction would be expressed by the equation—



Hydroxyamidosulphate decomposing under the influence of copper sulphate may give as little as 3½ per cent of its sulphur as dioxide. In all cases, the quantity of sulphur appearing as sulphate approximately equals that as amidosulphate. The production of any free nitrogen is still doubtful; it could only be formed when the sulphur as sulphate exceeded in amount that existing as amidosulphate.

*94. "The Degradation of Glycollic Aldehyde." By H. J. H. FENTON.

As glycollic aldehyde is now obtainable in a pure state (*Trans.*, 1895, lxvii., 774), experiments are being carried on with a view of studying its relationships and properties. The author showed that by means of Wohl's reaction formaldehyde may readily be obtained from glycollic aldehyde. Glycollic aldoxime is obtained as a syrup from the interaction of the aldehyde and hydroxylamine in alcoholic solution, but it has not been obtained quite pure. When this syrup is mixed with acetic anhydride and sodium acetate, a violent reaction takes place, and the acetyl derivative of glycollic nitrile (b. p. 177°) is formed. This is identical with that obtained by Henry (*Comptes Rendus*, 1890, cx., 759—760) from formaldehyde and hydrogen cyanide. When this acetyl derivative is acted upon by the calculated quantity of ammoniacal solution of silver oxide, silver cyanide separates in a crystalline state, and a product is obtained which, with dilute sulphuric acid, yields abundance of formaldehyde.

95. "Notes on the Chemistry of Chlorophyll." By LEON MARCHLEWSKI, Ph.D., and C. A. SCHUNCK.

The authors first discussed the absorption spectrum of unaltered chlorophyll, and conclude (1) that this spectrum is characterised by three bands between the lines B and F, and three between F and K β ; (2) that the bands exhibited by crude leaf extracts are caused by one chemical compound, chlorophyll, and not by several substances; (3) that no solution which does not exhibit this spectrum can be said to contain chlorophyll, no matter how it may have been prepared. Unaltered chlorophyll, by the action of hydrochloric acid, ought to give both phylloxanthin and phyllocyanin, the latter most certainly. The authors contend that Hartley's "blue chlorophyll" is not unaltered chlorophyll, but a derivative closely allied to alkachlorophyll, since its spectrum is quite different from that of unaltered chlorophyll, and gives with acids phyllotannin or its derivatives, but neither phylloxanthin nor phyllocyanin.

As to the several "chlorophylls," the authors corroborated the results of Hartley and Sorby's experiments, which tend to show the existence of a colouring-matter besides chlorophyll proper and the members of the xanthophyll group. They show, however, that Hartley's "yellow chlorophyll" is a mixture of this additional colouring-matter with members of the xanthophyll group, and that by removing the latter its colour is green; the name "yellow chlorophyll" is therefore unsuitable. Crude leaf extracts therefore contain two green colouring-matters, chlorophyll proper and another which is present only in small quantity; this exhibits a red fluorescence, and is characterised by an absorption band in the red which is more refrangible than that of true chlorophyll. The authors described a method by which chlorophyll could be obtained almost free from this green colouring-matter, and from the members of the xanthophyll group.

The action of bromine on phylloporphyrin and hæmatoporphyrin is very similar, and this is considered by the authors as an additional proof of the close relationship of these substances.

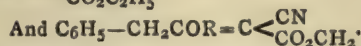
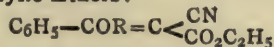
(To be continued.)

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

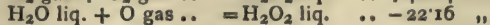
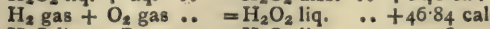
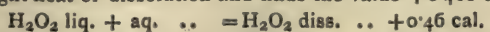
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 24, June 11, 1900.

The β -Phenyl and β -Benzyl α -Alcoyloxy- α -Cyano-acrylic Ethers:—



—A. Haller and G. Blanc.—The authors prepare these two ethers from their silver salts, and examine their properties.

Heat of Dissolution of Hydrogen Peroxide. Thermic Value of the Hydroxyl Function OH. Influence of Hydrogen and Carbon.—M. de Forcrand.—It has been found that it is just possible to obtain hydrogen peroxide almost in the anhydrous state by distillation under very reduced pressure. This fact proves that if the heat of dissolution of anhydrous H_2O_2 is positive, it is very slight. The author measures this slight heat of dissolution and finds the value +0.460 cal.



Further, he finds that for each of the two OH radicles, forming solid hydrogen peroxide, the value is +34.67 cal.

Direct Preparation of Crystalline Mercuric and Mercurous Iodide by the Wet Method.—F. Bodroux.—Crystalline mercuric iodide can be obtained by dissolving an excess of the amorphous substance in potassium iodide, or, better, in concentrated boiling hydrochloric acid. On cooling, the salt separates out in octahedra, or in quadratic prisms of a bright red colour. The yellow modification can be prepared either by sublimation or in the wet way by adding an excess of water to a solution of mercuric iodide in alcohol. The author observes that when a small quantity of ethyl or methyl iodide is left in contact with a large excess of a solution of a mercury salt at ordinary temperatures, mercuric iodide is produced. This experiment succeeds with the chloride, nitrate, and sulphate of mercury, but the finest crystals are obtained when the acetate is used.

The Impossibility of the Primary Formation of Potassium Chlorate obtained by an Electrolytic Method.—André Brochet.—The author's experiments show, in an absolutely clear and decisive manner, that during the electrolysis of alkaline chlorides, contrary to the hypothesis of Cettel, Haber and Grinberg, Foerster, Jorre, and Müller, the formation of the chlorate is never due to a primary action, but is always preceded by the intermediate formation of the hypochlorites, even in a very alkaline medium, and when the hypochlorite is not apparent.

Decomposition of Metallic Chlorides.—M. Echsner de Coninck.—The author continues his researches on the action of animal black on dilute aqueous solutions of HgCl_2 , CdCl_2 , Al_2Cl_6 , and SnCl_4 . Besides which, he makes new experiments with a dilute solution of Fe_2Cl_6 in water. This series of reactions, which are quite distinct from one another, are satisfactorily explained if it is allowed that animal black acts as a dialyser, and that the liquid contains, at any given moment, a modified oxide or hydrate of iron dissolved in hydrochloric acid. The animal black, which is in excess, takes up little by little the oxy-compound of iron, and hydrochloric acid passes into the filtrate. This explanation seems to conform with experiment, and also with the theoretical explanations which have been put forward by Graham, Debray, Krecke, and Kossel.

Hydrogenation of Acetylene in Presence of Reduced Iron or Cobalt.—Paul Sabatier and J. B. Senderens.—On comparing the actions of the various metals used in these experiments, copper, iron, and cobalt, on a mixture of hydrogen and acetylene, they are seen to present remarkable differences. The combination of two gases, with production of ethane, which accompanies a certain proportion of formenic carbides, is realised very easily by reduced nickel at ordinary temperatures, and also—but only when hot—by nickel. In the presence of excess of hydrogen, the amount of ethylenic carbides obtained is negligible. Copper acts less energetically, and gives a larger proportion of ethylenic carbides, whilst iron is the least active of all, and gives a very slight formation of ethane, whilst considerable quantities of free hydrogen are found in the gaseous product.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Selenium.—What is the best way to prepare metallic selenium of the variety that conducts electricity? The ordinary text-book methods give bad results.—R. R.

Gases from Coal.—Will you inform me of any articles on the chemistry of gases obtained from the destructive distillation of coal, and also on the practical means of obtaining tar, ammonium sulphate, benzol, and potassium cyanide as by-products of the coking of coal?—J. W. E.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2121.

ON RADIO-ACTIVE BARIUM.

By BÉLA v. LENGYEL.

AFTER the uranium rays of Becquerel had been discovered, and G. C. Schmidt had shown that the thorium compounds emit similar rays, Curie found in uranium ore (pitchblende) a radio-active substance whose radiation was about 400 times that of uranium. They predicted in this substance a hitherto unknown element, coinciding in its chemical reactions with bismuth, and which they called "polonium." They did not succeed in separating polonium from bismuth.

These same experimentalists, in conjunction with M. G. Bémont, isolated in the same year a more highly active substance from the pitchblende, in which they likewise predicted a hitherto unknown element that they called "radium." Radium possesses the chemical properties of barium, and is as inseparable from the latter as is polonium from bismuth. Demarçay examined the spectrum of radio-active barium, and found next to the intense barium lines a new line, which apparently belongs to radium. M^{me}. Skłodowska Curie determined the atomic weight of active barium, and found it eight units higher than that of inactive barium.

The existence of radium in radio-active barium compounds is established through the radio-activity, the spectrum, and the higher atomic weight.

F. Giesel likewise produced radio-active barium from pitchblende. He proceeded by a method quite different from that of Curie. Out of 1000 kg. of raw material he obtained 15 grms. of the preparation of radio-active barium. He also found some polonium combined with lead.

Finally, it may be remarked that Debierne had also isolated from pitchblende a very active substance, whose properties resemble those of titanium.

Many other experimentalists have worked at radio-active bodies; but their experiments were conducted almost exclusively with reference to the rays emitted by these bodies.

We thus know of radio-active bodies which have five different origins: the compounds of uranium, thorium, polonium, radium, and Debierne's substance resembling titanium. Uranium and thorium have been long known as chemically well-defined simple bodies; on the other hand, the three last-named are so far only hypothetical elements. Of these three hypothetical elements radium is the best known, as there are most accounts about it. The objective evidence of these accounts scarcely convinces one that radium is an existing element. For the existence of this element, two circumstances come principally into consideration from a chemical point of view, viz., the higher atomic weight of radio-active barium, and the spectrum of the same. M^{me}. Curie found the atomic weight of radio-active barium 8 units higher than that of the inactive, from which she concluded that radium must exist. But when we consider that radium, which so entirely resembles barium, must be divalent, and has as high an atomic weight as uranium, and, further, base our reckoning on the atomic weight of radio-active barium (145.8) found by M^{me}. Curie, it appears that the preparation from which the atomic weight was determined must have contained about 2 per cent radium chloride: that is a considerable quantity, and it cannot be assumed that such a quantity of a foreign element would not betray itself during the various chemical transformations.

Also, if a close chemical similarity between radium and barium is assumed, in consequence of which the two elements could not be distinguished and separated from each other by means of the usual analytical methods, it is yet difficult to accept radium as an existing element. Demarçay has examined the spectrum of radio-active barium and found in it only one line which was visible along with the intense barium lines, and which did not belong to barium. The spectra of calcium, strontium, and barium are of the same type; they consist of sharp lines and shaded bands; even the grouping of the lines and bands is alike. It was to be expected that radium, which is almost identically the same as barium, would show a similar spectrum.

Also, one must take into regard the fact that these new hypothetical elements are always found combined with other well-known chemical elements. M. and M^{me}. Curie found polonium combined with bismuth; Giesel with lead. Radium is combined with barium; Debierne's element with titanium. All these radio-active bodies have the same source, uranium pitchblende, from which they were separated by different analytical methods.

It can scarcely be maintained that chemical elements exist which are in no way distinguishable from other well-known ones, except in radio-activity; and it can scarcely be supposed that these elements, which can be transformed into various compounds, would in no single case give evidence of their presence in the chemical reactions but through their radio-activity.

Such considerations led me to examine experimentally the question as to whether the radio-active bodies contained new elements. After all the radio-active bodies known hitherto, which are said to contain a new element, were separated from the uranium pitchblende by analytical methods, I chose the synthetic method for the decision of the proposed question. For it is obviously clear that the question of radium being a chemical element must be answered in the negative as soon as it is found possible to transform ordinary inactive barium into the radio-active variety. At the same time this might be the synthetic production of radium.

My experiments carried out in this direction gave a positive result. It appeared that one can transform ordinary barium into a radio-active form which apparently possesses all the properties of radio-active barium observed by different experimentalists.

For the production of radio-active barium sulphate, the following should initially be noted:—Uranyl nitrate is melted together with 2 or 3 per cent barium nitrate, the nitric acid driven off as far as possible by sustained heating, and the remaining oxides fused in the electric arc. The fused mass is dissolved in nitric acid, and the solution evaporated, by which means a large portion of the baryta separates as nitrate. The hot solution is decanted from the crystals, diluted with three or four times its volume of water, and the radio-active barium sulphate precipitated with sulphuric acid. Only a small amount of sulphate is obtained in comparison with the quantity of barium nitrate used. I obtained, from 20 grms. barium nitrate, only 3 to 5 grms. sulphate, which is undoubtedly still largely mixed with ordinary barium sulphate.

The most favourable conditions for the production of radio-active barium are not yet determined. But the fact that a radio-active barium sulphate can be obtained as above described, seemed to me to be sufficiently important to publish in a preliminary notice.

I have so far prepared three compounds—radio-active barium sulphate, and from this the chloride and carbonate.

Radio-active barium sulphate is precipitated as a fine white substance, adhering rather readily to glass when the acid solution is treated with sulphuric acid or a sulphate. The precipitate, when well washed with hot water, dried, and heated, is white with a tinge of yellow, perhaps due to a trace of uranium. The substance was put into a little glass vessel, the bottom of which showed a faint gleam of light, and the glass placed on a sensitive

photographic plate, wrapped in black paper. After two hours the plate was developed, and a strong black mark appeared, corresponding to the transverse section of the glass. Hence the preparation was radio-active, and its activity increased after some days.

Radium rays are said to penetrate their metal sheets; my preparation of active barium sulphate emitted rays possessing the same property. One half of a copper coin was ground down to about one-third the thickness of the other half. The coin was laid between the vessel containing the barium sulphate and the sensitive plate, wrapped in black paper, and left there for three hours. After development, the plate was found to have remained white on the spot corresponding to the thicker copper layer, and had become grey beneath the thinner copper layer, of which there was an image surrounded with an intense black margin, indicating the action of the rays received direct on the plate beyond the copper coin.

Radium rays illuminate a barium platinocyanide screen; the rays of my substance exhibit the same property, though in less degree. The air becomes an electrical conductor by means of radium rays, and the same is the case with my prepared active barium sulphate. The carbonate and chloride prepared from the active sulphate were also active.

This is, so far, the limit of my researches. They do not nearly suffice to decide the question as to whether radium is an existing chemical element, or not; but those facts render doubtful the existence of radium. The question can only be settled by a searching examination, and I have in hand the preparation of the necessary material in sufficient quantity to be able to undertake this examination.

Chemical Laboratory of the University, Budapest II.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART III.

By HARRY BREARLEY.

(Continued from p. 19).

CARBON (*continued*).

III. ESTIMATING THE LIBERATED CARBON.

III.a. Weighing the Dried Residue.—

372. EGGERTZ (*C. N.*, vii., 254).—Iron separated with iodine and dried residue weighed, or Fe separated with CuCl_2 and residue combusted. Graphite separated with HCl ; residue dried, weighed, and ignited. Describes also the colour process and some of its limitations. Later (*C. N.*, xlv., 173) uses iodine dissolved in ferric iodide for separating the carbon.
373. WITTSTEIN (*C. N.*, xxii., 311).—Dissolve in $\text{CuSO}_4 + \text{CuCl}_2$, weigh dried residue. Loss on ignition = C (see 368).
374. BOUSSINGAULT (*C. N.*, xxii., 317).—Separates with HgCl_2 (339); ignite residue at dull red; loss = carbon. Ignite in O current; loss = graphite.
375. HEID (*C. N.*, lxxvi., 183).—After treating with alcohol and ether, the residue, dried at 120°C ., is ignited; loss = C. Graphite estimated similarly.
376. DOUGHERTY (*C. N.*, lxxx., 121, 146, 242, and 266).—Liberated carbon washed with hot dilute HNO_3 , dried, and ignited; loss $\times 0.675$ = C. Graphite similarly. Not available for FeMn.

III.b. Dry Combustion of the Residue.—

377. ABEL (*C. N.*, vi., 133).—Dissolve in acid CuCl_2 (see 351), and burn residue with CuO . Liberate graphite with HCl , separate SiO_2 with KHO , dry, and weigh.

378. TOSH (*C. N.*, xvi., 67).—Describes Regnault's (combustion with PbCrO_4 and KClO_3), Fresenius's (dissolve in H_2SO_4 , pass gases over CuO , and estimate C in residue), Wohler's (separation of Fe with Cl , and combustion of the residue), and Weyl's (334). Critical remarks on each process.
379. FORBES (*C. N.*, xvi., 105).—Mainly like Abel (377). Dissolving for ten days.
380. PIESSE (*C. N.*, xxviii., 198).—Decompose with warm acid cuprasodium chloride (see 354). Burn residue with CuO .
381. TURNER (*C. N.*, lii., 15).—Decompose with cuprammonium chloride (see 483). The filter-tube is also the combustion-tube when resting on a small sheet-iron stand.
382. CLEMENCE (*C. N.*, xlviii., 206).—Also burns the C in the (platinum) filtering-tube.
383. DEVILLE and TROST (*C. N.*, vii., 294).—Platinum tubes are porous to gases and vapours at high temperatures.
384. LANGLEY (*C. N.*, lxii., 218, and *J. I. S. I.*, 1890, ii., 583).—"International Standard's" work. The CO_2 is purified with CuO , Ag , AgSO_4 or CuSO_4 pumice, and CaCl_2 before being absorbed. An acid Cu solution gives higher results than a neutral one. Anhydrous CuSO_4 pumice soon becomes inefficient.
385. SHIMER (*C. N.*, lxiv., 43).—Akin to Langley's paper. Direct combustion of the same samples. After liberal use of HCl all chlorides may be washed from the C residue.
386. DROWN (*C. N.*, lxix., 4).—Oxygen passed over hot CuO before using. Cl retained by Ag , FeSO_4 , and anhydrous CuSO_4 . KHO bulb absorbs all the CO_2 (see 413), and CaCl_2 prolong all the moisture.
387. SHIMER (*J. S. C. I.*, 1899, 863).—The combustion is successfully made in an ordinary platinum crucible fitted with a water-cooled stopper. Apparatus serviceable for other operations generally requiring a tube.
388. DUPRÉ and HAKE (*C. N.*, xliii., 69).—Absorb CO_2 in baryta water, convert BaCO_3 to BaSO_4 . BaSO_4 weighs 19.4 times as much as the original carbon.
389. GOOCH and PHELPS (*C. N.*, lxxii., 194).—Estimation of CO_2 as in 388. Special apparatus to collect CO_2 . BaCO_3 washed under a protecting layer of xylene.
390. PHELPS (*C. N.*, lxxiv., 65).—Estimates excess of $\text{Ba}(\text{HO})_2$ with iodine and arsenious acid.
391. RICHARDSON (*J. C. S.*, lxx., 469).—Apparatus for absorbing CO_2 in $\text{Ba}(\text{HO})_2$.
392. HANDY (*J. I. S. I.*, 1895, ii., 589).—Absorbs CO_2 in $\text{Ba}(\text{HO})_2$, and weighs BaCO_3 or titrates excess with H_2SO_4 .
393. MOISSAN (*C. N.*, lxxii., 2).—Carbon is separated from Mo with Cl , and the residue combusted; or sample decomposed with acid in a stream of oxygen which passes over CuO into KHO . The graphite is determined in the residue.
394. BENNEVILLE (*J. I. S. I.*, 1895, i., 230).—C liberated with Cl , mixed with PbCrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, and burned.
395. BLOUNT (*C. N.*, lvii., 27).—Irregular results of Fresenius's process (378) due to formation of liquid hydrocarbons (see 369 and 371).
396. PHILLIPS (*J. I. S. I.*, 1887, ii., 372).—A solution of KHO in glycerin is used to absorb CO_2 .
397. BAKER (*J. C. S.*, li., 253).—Carbon containing moist oxygen gives rise to CO_2 when heated at 100°C .
398. STOKES (*C. N.*, lvii., 150) uses asbestos instead of clay tiles, and an iron combustion tube closed with brass cap and leaden washer.
399. JERVIS (*C. N.*, lxxvii., 5).—Arched asbestos cover for combustion furnace.
400. WHITE (*C. N.*, xlv., 65).—An asbestos stopper made by pressing the moistened fibres into a mould.
401. DROWN (*C. N.*, lvii., 223).—Uses a funnel with so

wide a stem that the dried asbestos and residue can be pushed down it into the combustion tube.

402. BRENNEMAN (C. N., xlviii., 168).—A platinum cylinder fitted with a perforated disc acts both as filter and boat.
403. CARIUS (C. N., liii., 66).—The CO_2 is freed from SO_2 by passing through heated PbCrO_4 .
404. ETARD, (C. N., xlvii., 178). Uses pumice soaked with $\text{Cu}(\text{NO}_3)_2$, and ignited to provide the CuO .
405. KNOP (C. N., iv., 13).—Collects rapidly evolved CO_2 in a rubber bag, and subsequently passes it through KHO (see C. N., lxxv., 241).
406. RUSSELL (C. N., xvii., 260).—Indiarubber absorbs notable amounts of CO_2 .
407. WILLIAMS (C. N., xliii., 69).—Black rubber is very pervious to CO_2 . See also KOBBE (Z. S. C. I., 1890, 1072).
408. EILOART (C. N., lviii., 284).—The calorimetric bomb suggested as a combustion-furnace.

III.c. Wet Combustion of the Residue.—

409. ELLIOT (C. N., xix., 152).—Liberate C with CuSO_4 and acid CuCl_2 , and burn residue with CrO_3 and H_2SO_4 .
410. CAIRNS (C. N., xxv., 271).—Oxidation with CrO_3 used for graphite and for varieties of coal. See also Wiesner (Z. C. S., lxii., 1273).
411. PACKER (C. N., xxviii., 282).—Like 409. CO_2 passed through H_2SO_4 into the KHO . (See 332 and 414).
412. LANGLEY (C. N., lxii., 219).—"International Standards" work. A chlorine compound passes both AgSO_4 and anhydrous CuSO_4 into the KHO . Precautions devised.
413. PARRY and MORGAN (C. N., lxvii., 175).—Liberate C with neutral and acid cuprammonium chloride. A little CO_2 passes the Geissler bulb, and is retained by soda-lime (see 386).
414. SARNSTRÖM (Z. I. S. I., 1886, 1016).—The iodine carbon residue (372) is not of constant composition, and hydrocarbons are evolved during the dissolving. Hydrocarbons are evolved during combustion with CrO_3 ; these are burned to CO_2 with CuO .
415. GALBRAITH (Z. I. S. I., 1897, i., 567).—A process like Sarnström's.
416. KONINCK (Z. C. S., liv., 1341).— AgSO_4 added along with the CrO_3 prevents even a trace of chlorine being evolved.
417. BLUM (C. N., lx., 167).— AgSO_4 does not retain the chlorine if strong H_2SO_4 is used.*
418. AUCHY (Z. S. C. I., 1898, 604).—The KHO should have a sp. gr. of 1.40. Occasionally chlorochromic compound not oxidised by Langley's "pyro" (412) are formed. In the wet combustion of graphite CO is given off.
419. AUCHY (Z. C. S., lxxiv., ii., 534).—The error due to condensation of moisture on the KHO bulb cannot be allowed for by using a "dummy" bulb.
420. WIDMER (C. N., lxii., 274).—The C of organic bodies is not completely oxidised to CO_2 by CrO_3 and H_2SO_4 . Some CO is formed.
421. LUDWIG (C. N., xxv., 227).— CO is readily oxidised to CO_2 by saturated solutions of CrO_3 .
422. ALLEN (C. N., lviii., 21).— CO_2 is always evolved on heating pure H_2SO_4 and commercial CrO_3 .
423. PHELPS (C. N., lxxvi., 256).—Oxidises many organic bodies with CrO_3 , and after acting on Ludwig's suggestion, estimates the CO_2 . Estimates the combined oxygen also, by titrating the residual CrO_3 .
424. ANON. (Z. S. C. I., 1886, 617).—Combustion with

CrO_3 . Chlorine is absorbed by powdered metallic antimony,

425. LORD ("Metallurg. Anal.," p. 62).—The proper strength of H_2SO_4 in the mixture is from 50 to 70 per cent. Fused CaCl_2 usually contains CaO , and so can absorb CO_2 in the drying tube.

III.d. Volumetric Estimation of the Carbon.—

426. PARRY (C. N., xxv., 301).—Residue combusted with CuO in vacuum and CO_2 measured. Direct combustion of Fe gives low results.
427. IMBERT and COMPAN (C. N., lxxix., 267).—Carbon (lamp-black) is digested with H_2SO_4 and CrO_3 , and residual CrO_3 estimated with KI and $\text{Na}_2\text{S}_2\text{O}_3$.
428. J. T. (C. N., lxxx., 52 and 210).—Carbon liberated with Cu solution may be estimated by a modification of the above process, but not if Cr is present. Combined C is oxidised most rapidly by mixtures containing 50 to 70 per cent H_2SO_4 , and graphite by mixtures containing 90 per cent H_2SO_4 . Mixtures of $\text{K}_2\text{Cr}_2\text{O}_7$ containing 60 per cent or over of H_2SO_4 are slowly decomposed at 100° C.

(To be continued).

EIGHTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its Eighteenth Annual Report, covering the nine months ending June 1, 1900.

Works Published.

"Index to the Literature of Zirconium." By A. C. Langmuir and Charles Baskerville. Smithsonian Institution, Washington City, 1899. 29 pp. 8vo.

This forms No. 1173 of the Smithsonian Miscellaneous Collections. The chronological list of references is followed by a Matter-index.

"A Bibliography of Steel Works Analysis." By Harry Brearley. CHEM. NEWS, lxxx., 233 *et seq.* (Nov., 1899).

The partial bibliography is confined to the contents of three English journals: CHEM. NEWS, Journ. Chem. Soc. (London), and Journ. Iron and Steel Inst.

The Committee also chronicles the publication of these foreign bibliographies:—

"Führer durch die gesammte Calcium-Carbid und Acetylen-Litteratur." Bibliographie der auf diesen Gebieten bisher erschienenen Bücher, Journale, Aufsätze in Zeitschriften, Abhandlungen und wichtigeren Patentschriften. Herausgegeben unter Mitwirkung von L. Ludwig. Berlin, 1899. 8vo.

This covers the industrial field as fully as the bibliography by Mathews does the scientific field, and both taken together are important for students of the subjects.

"Répertoire générale, on Dictionnaire méthodique de Bibliographie des Industries Tinctoriales et des Industries annexes depuis les origines jusqu'à la fin de l'année 1896." Par Jules Garçon. Paris, 1899-1900.

The first volume of this extensive work contains a chapter on the sources of chemical bibliography, in which the author fully recognises the works issued under the auspices of this Committee and those published by the Smithsonian Institution. The author writes:—"America yields to no nation in the matter of bibliography; an

* Blum says, "According to Volhard, H_2SO_4 , diluted with half its volume of water, does not attack AgCl . This, however, is a degree of dilution which never occurs in the combustion of carbon in irons." It has since been shown that sulphuric acid, even more dilute than Volhard's, effects the combustion most rapidly. (See 425 and 428).

* Advance proofs from the Proceedings of the American Association for the Advancement of Science, 1900, vol. xlix.

American devised the decimal system of bibliography, and Americans formed the Committee on Indexing Chemical Literature, of which the Reports, edited by Mr. H. C. Bolton, are found in the *Proceedings of the American Association for the Advancement of Science*, since 1883.

Reports of Progress.

Dr. Alfred Tuckerman has completed and sent to the Smithsonian Institution a Supplement to his "Index to the Literature of the Spectroscope," which covers the period from 1887 to 1899.

Dr. H. Carrington Bolton's *Second Supplement* to his "Select Bibliography of Chemistry," containing a list of 7500 chemical dissertations, is passing through the press; it will form a volume of the Smithsonian Miscellaneous Collections.

Mr. A. G. Smith, of Cornell University, is engaged on an "Index to the Literature of Selenium and Tellurium," which, it is expected, will be completed this summer.

Dr. Frank I. Shepherd, Secretary of the Cincinnati Section of the American Chemical Society, plans a bibliography of the *alkaloids*.

Mr. Frank R. Fraprie, of the University of Illinois, Urbana, Ill., writes to the Committee that he contemplates preparing an "Index to the Literature of Lithium."

The Committee chronicles the new method of indexing chemical substances used by M. M. Richter in his "Lexicon," and by the editors of the *Berichte der Deutschen Chemischen Gesellschaft*, in which the references to organic compounds are arranged under their empirical formulæ; the Chairman of your Committee finds that Mr. Edwin A. Hill, of the U.S. Patent Office, has been engaged for more than two years in cataloguing chemical bodies under their empirical formulæ for convenience of his office. Mr. Hill's system is adaptable to inorganic compounds as well as to those of carbon, and differs from the German plan in arrangement of the symbols, being much simpler. This method will be explained in print before long.

It is gratifying to note the increasing and continued interest in bibliography on all sides, and the Committee stands ready to encourage the movement in chemistry by practical assistance to those desirous of contributing to now considerable list of indexes. Address correspondence to the Chairman, at the Cosmos Club, Washington, D.C.

Committee:—

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
A. R. LEEDS,
A. B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

CRYSTALLISATION OF STEEL AND IRON.

By JOHN PARRY.

THE freezing or solidification of fluid iron may very well be compared with the freezing of water. The tendency in both cases is to assume the crystalline form.

But the crystalline structure in the case of ice is not very apparent in the mass or block of ice; it presents an apparently amorphous structure, the crystals being so closely packed together.

Graham, however, states that the ice may exist in the colloid (non-crystalline form) and in the crystalline form. Colloid ice is formed in contact with water at 0° C., and it has the elasticity seen in all colloid or non-crystalline bodies: on the contrary, when water is frozen at few degrees under zero, it has a well-marked crystalline structure.

It would appear that, judging from recent research,

something like this occurs in manipulating and heating steel, more especially very soft metal, containing less than one-tenth carbon; and a study of the fracture of steel, variously heated, induced me to say, many years ago, that the freezing of water and the freezing (or solidification) of steel, were comparable phenomena—the water, of course, at the normal temperature of fluidity, and the steel at the usual point of fusion or fluidity.

As regards the apparent amorphous ice previously referred to, Prof. Tyndall has shown that, by passing a pencil of solar rays through a sheet of ice, as the ice fuses, well-defined crystals are gradually developed, and may be seen on the screen.

On cooling, of course the reverse phenomena may be observed: further it is clear that, if the heating or cooling is suddenly stopped at any given period, the mass, strictly speaking, cannot be in the original amorphous state (*i. e.*, fine-grained). So far as I am able to follow the vast mass of facts recently placed before us, bearing on the changes in the structure of steel, it seems probable that these are explainable by the same laws as govern the freezing of water, or the gradual fusion of ice under the varying conditions above referred to. There can, I think, be little doubt that brittle weak steel is thus at times manufactured from metal of irreproachable chemical composition.

Newport, Mon., July 10, 1900.

ON THE ACTION OF IODIDES AND OF HYDRIODIC ACID ON SULPHUROUS ACID.

By A. BERG.

THE recent publication of a paper by M. Péchard in the *Comptes Rendus* (vol. cxxx., p. 1188) has decided me to make known the results I obtained in my research on the action of iodides and hydriodic acid on solutions of sulphurous anhydride, a research commenced in 1899 and temporarily put on one side through stress of other work.

The yellow colouration taken by solutions of iodides in the presence of sulphurous acid, which I recognised not to be due to the presence of free iodine, caused me to suspect the formation of a dissociable compound of these two bodies.

M. Péchard's work has fully confirmed this suspicion.

What I want particularly to draw attention to in this paper is the ulterior reaction of the iodides and of hydriodic acid on sulphurous acid, a reaction which is not mentioned by the above-named author.

The yellow liquid, when left to itself, slowly deposits a powder formed of small spherical grains of sulphur, and sulphuric acid is found in the liquid. At the same time the colour of the liquid becomes gradually fainter, and finishes by disappearing completely. This reaction is so much the slower as the quantity of iodide or hydriodic acid used is less.

On the 25th March, 1899, I closed up, in a series of sealed tubes, equal quantities (20 c.c.) of a solution of sulphurous anhydride in boiled water, to which were added decreasing quantities of iodide of potassium. One of the tubes contained no iodide, and served as a check. The whole of them were left in a part of my laboratory which received direct sunlight for a portion of the afternoon.

	Numbers of the Tubes.					
	1.	2.	3.	4.	5.	6.
	Grm.	Grm.	Grm.	Grms.	Grms.	Grms.
Quantity of iodine..	0.1	0.5	1	2	4	8

On the 31st of March tube No. 1 commenced to deposit sulphur, and the colouration of the liquid became fainter and fainter, until, on the 5th of April, it had entirely disappeared.

Tube No. 2 did not commence to become cloudy until the 4th of April, and complete decolouration did not take place until the 21st of April.

Tube No. 3 became cloudy on the 12th of April, and colourless on the 17th of May.

Tube No. 4 became cloudy on the 22nd of April, and colourless much later (some time in September during my absence).

Finally, tubes Nos. 5 and 6 did not lose their transparency until the 4th of May for the first, and the 12th of June for the second, and are still to this day decidedly yellow in appearance.

In all these tubes a plentiful deposit of sulphur was found. On opening them, not a trace of sulphurous acid can be found in the colourless liquids. At the same time a scarcely perceptible odour of sulphuretted hydrogen can be observed, it is otherwise impossible to detect.

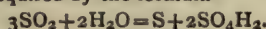
The solutions which are not completely decolourised still contain a small quantity of sulphurous acid.

The estimation of the deposited sulphur and of the sulphuric acid formed gives the following figures:—

	Numbers of the Tubes.		
	1.	2.	3.
Sulphur deposited	0.234 grm.	0.250 grm.	0.251 grm.
Sulphuric acid ..	1.487 grms.	1.490 grms.	1.380 grms.
Sulphur in the sulphuric acid ..	0.486 grm.	0.487 grm.	0.451 grm.

As for the check tube it did not undergo any change, and analysis showed that it contained 0.702 grm. of sulphur in the form of sulphurous acid.

We thus see that the precipitated sulphur and that of the sulphuric acid formed are practically in the proportion of 1 to 2, as required by the formula—



There are, however, no further reactions, for we find, either in the free state or in the form of sulphuric acid, the whole of the sulphur in the sulphurous acid used.

Light having appeared to take part in the phenomenon, on the 10th of April I prepared two similar tubes to No. 1 in the above series. I placed them in a continuous current of water in a light place, after having wrapped one of them up in a sheet of lead. On the 20th of April the tube exposed to the light was completely decolourised, while the other one was intact and showed no trace of any deposit. However, when left for a long time in the dark, it eventually lost its colour.

Light is not therefore a necessary factor in the reaction, but only acts by accelerating it. The blue and violet rays are the most active, the red rays behave almost the same as complete darkness.

Heat also acts as an accelerating agent, for of two tubes placed in darkness—one at the ordinary temperature and the other kept at 95°—the first took a long time to become decolourised, while the second lost its colour very rapidly.

Hydriodic acid behaves in the same manner as iodide of potassium, and is found unaltered at the end of the reaction, while in the case of the iodide, sulphate of potash is formed.

A small quantity of hydriodic acid or of iodide is thus likely to destroy, in the long run, large quantities of sulphurous acid; the yellow compound formed in the first place becomes decomposed, forming sulphur, sulphuric and hydriodic acids, or iodide, which may again react on a fresh portion of sulphurous acid.—*Bull. Soc. Chim.*, Series 3, xxiii., No. 12.

Action of Acetylene on Cuprous Chloride dissolved in a Solution of Potassium Chloride.—M. Chavastelon. —The author finds that a prolonged action of acetylene on cuprous chloride, dissolved in potassium chlorate solution, causes the formation of colourless crystals amongst the yellow ones. These are orthorhombic in form.—*Comptes Rendus*, cxxx., No. 24.

DIAGRAM OF COMPOSITION OF IGNEOUS ROCKS.

By H. WARTH.

RECENT studies about the average chemical composition of larger numbers of igneous rocks in the aggregate have shown that figures obtained from any one hundred or more samples are very similar, in fact practically equal. (See A. Harker, "On the Average Composition of British Igneous Rocks," *Geological Magazine*, May, 1899, No. 5). This will be found also the case when comparing the

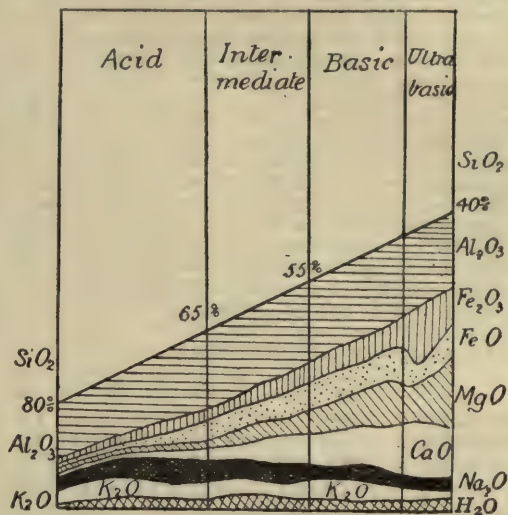


DIAGRAM-FIG. 1.

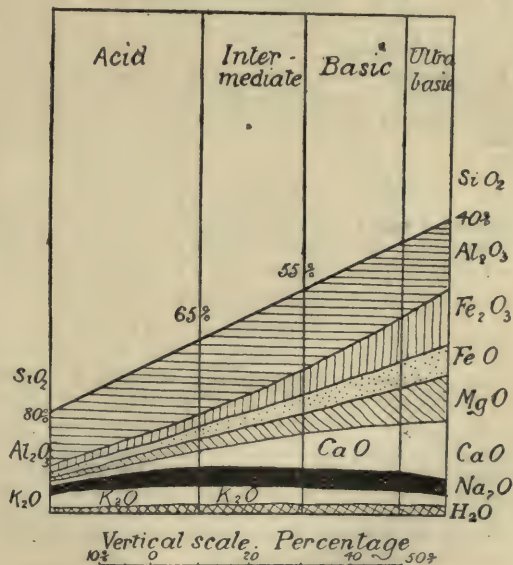


DIAGRAM-FIG. 2.

following average, which I calculated from the analysis of igneous rocks compiled by Roth in his "Petrographie der plutonischen Gesteine."

Now if it is of interest to discuss these average results, notwithstanding the wide discrepancies of many individual compositions, it may also be worth while to find out how on the average the compositions vary with the relative

acidity of the rocks. For this purpose I have arranged the bulk of Roth's samples in the order of acidity, and after calculating average compositions of eighteen groups of closely approaching acidity, I constructed from the figures the subjoined diagrams. The first diagram (Fig. 1) shows the actual results, the second (Fig. 2) shows them rounded off.

The percentage of silica varies from 80 to 40, and the usual limits between acid, intermediate, and basic rocks are indicated by the vertical lines on the diagrams. The diagrams show the percentage of the different bases which corresponds with the percentage of silica, indicated on the straight diagonal boundary-lines of the silica, which rise from the points marked 80 per cent on the left of each diagram to the points marked 40 per cent on the right of each diagram. As it would not be possible to give so many details on the diagram, small quantities of other acids have been reckoned with the silica and treated as such. These acids are titanatic acid, phosphoric, carbonic, and in rare cases also sulphuric acid. In the case of the bases I also included the manganous oxide, and a few other rarer metallic oxides with the ferrous oxide. The total number of specimens which were calculated amounted to 428. About sixty-six of Roth's analyses were omitted, partly because they referred to strongly weathered specimens, and partly to exclude serpentines and some other more purely magnesian silicates. The specimens as given by Roth are from generally distributed localities, and the following are the compositions of extremes and of the total average in numerical figures:—

	Si	Al	Fe	Fe	Mg	Ca	Na ₂	K ₂	H ₂
Most acid ..	79.7	11.4	1.1	0.3	0.7	0.9	2.6	2.5	0.8
Most basic ..	40.0	12.3	10.2	5.8	14.2	10.5	3.1	1.2	2.3
Average..	58.3	15.3	5.0	3.6	4.0	5.9	3.4	3.0	1.5

The diagrams show the alumina to be nearly constant, only slightly diminishing towards both extremes. The soda is also tolerably constant, diminishing slightly at both ends. The potash is decidedly stronger at the acid end, whilst the other oxides increase from left to right, so as to show quite a fan-like expansion from the acid end towards the basic end.

The diagrams show also that the arbitrary boundaries between acid, intermediate, and basic rocks are very suitably chosen.—*Geological Magazine*, vii., No. 432, June, 1900.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, July 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 200 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 200 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The deficit in rainfall registered during the last three months has now given way to an excess. The rainfall at Oxford during June was 2.73 inches; the average fall for this month is 2.11 inches; this gives an excess for the month of 0.62 inch, making the excess for the first six months of this year 0.96 inch, or 8.7 per cent on the thirty years' average.

Our bacteriological examinations of 523 samples have given the results recorded in the following table; we have also examined 37 other samples, from special standpipes, &c., making 560 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	95
New River, filtered (mean of 131 samples) ..	8
Thames, unfiltered (mean of 25 samples) ..	1677
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 283 samples) ..	9
Ditto ditto highest	169
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	221
River Lea, from the East London Company's clear-water wells (mean of 34 samples) ..	11

Of the 460 samples of filtered water supplied to London, examined bacteriologically during the last month, less than 1 per cent has been found to contain above 100 and below 170 microbes per c.c. This demonstrates that the London supply more than maintains its normal good quality.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE EIGHTH GROUP OF THE PERIODIC SYSTEM AND SOME OF ITS PROBLEMS.*

By JAS. LEWIS HOWE.

(Continued from p. 17).

THE episode of the discovery of palladium throws a curious light upon the chemistry and chemists of that period. On May 12, 1803, Chenix read a paper before the Royal Society (*Phil. Trans.*, 1803, xciii., 200), stating that two weeks previously (April 29) he learned by a printed notice that a substance announced as palladium, a new metal, was offered for sale at the establishment of a well-known mineralogist. The printed notice (*Ann. de Chim.*, 1803, xlvii., 333) opens: "Palladium, or new silver, has these properties among others which show it to be a new noble metal," and then follows the enumeration of eight characteristics of the metal, closing with the address where the new metal could be bought. Chenix goes on to say that the mode adopted to make known a discovery of so much importance without the name of any creditable person, except the vendor, appeared to him unusual, and not calculated to inspire confidence. Having examined a small sample, Chenix returned and purchased the whole supply. He then says: "We shall cease to wonder at what has been related by these chemists (Berthollet on affinity, and Hatchett on alloys), when we learn that palladium is not, as was shamefully announced, a new simple metal, but an alloy of platina; and that the substance which can thus

* An Address delivered before the American Association for the Advancement of Science, New York Meeting (1900), Section C.

mask the most characteristic properties of that metal, while it loses the greater number of its own, is mercury. Chenivix, however, on May 4, had written (*Ann. de Chim.*, 1803, xlv., 333) to Vauquelin that palladium really was a new metal, and Chenivix sent him a small specimen. A few days later another letter (*Ann. de Chim.*, 1803, xlv., 336) makes the claim that palladium is a platinum-mercury alloy. The editors of the *Annales* comment upon this, that from Vauquelin's experiments Chenivix is probably wrong. It is interesting to read the comments of Chenivix upon the masking of the individual properties of both platinum and mercury in palladium,* a correct moral drawn from a false premise. There was something almost prophetic in the observations of Chenivix, for there are in chemistry no elements whose properties exhibit such great variability when not pure as do those of the platinum group.

The still anonymous discoverer of palladium immediately offered, through *Nicholson's Journal*, a reward of twenty pounds sterling to any one who should manufacture even twenty grains of real palladium,† and many chemists entered into the discussion as to the elementary character of the metal. On June 24, 1804, three days after Tennant had made known the discovery of iridium and osmium, Wollaston read a paper before the Royal Society (*Phil. Trans.*, 1804, xciv., 419), acknowledging himself to be the discoverer of palladium. Wollaston had been engaged in an effort to obtain malleable platinum, and having precipitated his solution of the ore with iron, he found a part of this precipitate to be soluble in a mixture of hydrochloric acid with saltpetre, potassium chloropalladate being formed. He at once concluded that palladium must be a simple metal, because there is "no instance in chemistry of a distinctly crystallised salt containing more than two bases combined with one acid," another correct conclusion drawn from a false premise. In his solution Wollaston found also indications of rose-coloured soluble crystals, which he attributed to another new metal, and to this he gave the name rhodium. This is the explanation of his curious method of making known his discovery of palladium: "On this and on other accounts I endeavoured to reserve to myself a deliberate examination of these difficulties, which the subsequent discovery of a second new metal, that I have called rhodium, has since enabled me to explain, without being anticipated even by those foreign chemists whose attraction has been particularly directed to this pursuit" (*Nicholson's Journal*, 1805, x., 204). It is possible from this that Wollaston himself had been led

to his work, in part at least, by the earlier observations of the French chemists.*

It was in 1803 that Collet-Descotils had read a paper before the Institute of France on the cause of the different colours which affect certain salts of platinum. The residue from the solution of platinum ores in aqua regia, and which was thought to be graphite, was still slightly soluble in aqua regia, and gave a reddish tint to the potassium chloroplatinate made from it. The metal derived from this red salt was found to be only partially soluble in aqua regia, and hence, beyond question, Descotils had in hand on several occasions a fairly pure iridium, containing, however, in addition to platinum, perhaps traces of rhodium. He was convinced that he had here a new metal, but he did not investigate its properties.†

The same day that Descotils spoke before the Institute, a second paper on the same subject was presented by Fourcroy and Vauquelin. After extracting the platinum from the ore by aqua regia, they fused the residue with potash, and then treated it with acid. These chemists noticed that the potash was coloured orange-yellow, but ascribed it to the presence of chromium. They thus missed the discovery of ruthenium, which was to be separated several decades later by Claus. They noticed also on one occasion that the black powder which consisted of iridium and allied metals was apparently volatile, not recognising osmium, the cause of the phenomenon. In their second memoir they had iridium fairly pure, and they, too, noticed the rose colour of the double salt, but did not investigate the cause, which is the presence of rhodium.

It was reserved for Tennant the following year to describe clearly the separation of iridium and osmium from the platinum residues, and to name the one from the many different colours through which its chlorides pass, and the other from the intolerable odour of its tetroxide, OsO₄.

This osmium contained ruthenium, but this was overlooked by Tennant, as it had been by Fourcroy and Vauquelin. A few years later Vauquelin (*Ann. de Chim.*, 1814, lxxxix., 241) notes that osmium solutions give a beautiful blue colour when reduced by zinc, this being a characteristic reaction, not of osmium, but of ruthenium. At a still later date Berzelius noticed the orange-colour of the fusion of ruthenium with potash and saltpetre, but he attributed it to iridium.

It was in 1828 that the next effort was made to add to the number of the platinum metals. Professor Osann, of the University of Dorpat, announced (*Pogg. Ann. der Phys.*, 1828, xlii., 287) the discovery of a new metal in the platinum residues. He obtained long reddish prisms, with high lustre, which were easily volatile, and which Berzelius pronounced to be new. He had only 0.3 grm., and never obtained any more. The metal in these crystals he named *ruthenium*. They may have been an impure mixture of the tetroxides of ruthenium and osmium. In the next volume of the *Annalen* (*Pogg. Ann. der Phys.*, 1828, xiv., 340) he transfers the name ruthenium to another new metal with a golden lustre, and at the same time he mentions two other new metals, *pluran*, named from pl (atina) and ur (al), which is not further described, and *polin*

* "The substance which has been treated of in this paper must convince us how dangerous it is to form a theory before we are provided with a sufficient number of facts, or to substitute the results of a few observations for the general laws of nature. If a theory is sometimes useful, as a standard to which we may refer our knowledge, it is at other times prejudicial, by creating an attachment in our minds to preconceived ideas, which have been admitted without inquiring whether from truth or from convenience. We can easily correct our judgment as to facts, and the evidence of experiment is equally convincing to all persons. But theories, not admitting of mathematical demonstration, and being but the interpretation of a series of facts, are the creatures of opinion, and are governed by the various impressions made upon every individual. Nature laughs at our speculations; and though from time to time we receive such warnings as should awaken us to a due sense of our limited knowledge, we are presented with an ample compensation in the extension of our views and a nearer approach to the immutable truth"—*Phil. Trans.*, 1803, xciii., p. 317.

† "Dec. 19, 1803, Editor *Nicholson's Journal*. Sir: As I see it said in one of your Journals, that the new metal I have called palladium is not a new noble metal as I have said it is, but an imposition and a compound of platina and quicksilver, I hope you will do me the justice in your next and tell your readers I promise a reward of 20*g*, now in Mrs. Foster's hands, to any one that will make only 20 grains of real palladium, before any three gentlemen chymists you please to name, yourself one if you like. That he may have plenty of his ingredients, let him use 20 times as much quicksilver, 20 times as much platina, and in short of anything else he pleases to use: neither he nor I can make a single grain. Pray be careful in trying what it is he makes, for the mistake must happen by not trying it rightly. My reason for not saying where it was found was that I might make some advantage of it as I have a right to do. . . . I hope a little bit of whatever is made may be left with Mrs. Foster."—*Nich. J.*, 7, 1804, lxxv., 159.

* Since this Address was in type, I have received the interesting Presidential Address of Dr. Thorpe to the Chemical Society (London), in which this episode is treated quite exhaustively. What Wollaston's motive was in bringing his discovery to the notice of the scientific world in so extraordinary a manner, Dr. Thorpe says can only be surmised. Is not, however, in view of Wollaston's statement, the motive clearly apparent? He had found palladium; he was in pursuit of rhodium; he knew that at least four other distinguished chemists were also on track of new metals in platinum residues, and any hint, such as the publication of his work on palladium, would help them to anticipate him in the matter of rhodium, while if he kept silence some of them could not fail to discover palladium.

† Of this Descotils writes (*Ann. de Chim.*, 1803, xlviii., p. 165:—"On peut déjà conclure que la coloration en rouge des sels de platine est due à l'oxygénation d'une substance qui diffère du platine, et qui présente, lorsqu'elle est à l'état métallique, une grande résistance à l'action des acides."

(πολιος, grey), a grey metal of whose independent existence he seems to have some doubt. Polin was impure iridium with, perhaps, some ruthenium; plurin was quite possibly a mixture containing some ruthenium; the following year (*Pogg. Ann. der Phys.*, 1829, xv., 158), Osann acknowledged the metal to which the name ruthenium had been given to be a mixture of the oxides of titanium, zirconium, and silicon.

Fifteen years pass, and there appears at the University of Kazan, almost on the far eastern frontier of Russia, a chemist, Claus, who is destined to make greater contributions to the chemistry of the platinum metals, not only than those who had preceded him, but than any one of those who have lived in the nearly forty years since his death. Claus was fortunate in having at his disposal an almost unlimited quantity of platinum residues, from the stock which had accumulated at St. Petersburg during the period of the coinage of platinum. In spite of no considerable effort, I have failed to verify the tradition that the great mass of these residues was sunk in the Neva to prevent their use in debasing the coinage, and I am inclined to think that the greater portion was distributed to chemists, of which Claus received by far the largest share. In his first publication (*Bull. Akad. St. Petersb.*, 1845, iii., 38), Claus announces the discovery of a new metal, which he calls ruthenium, for the purpose of honouring Osann, whose ruthenium had failed to prove itself an element. It may be mentioned that Osann hardly appreciated the compliment, for he attacked Claus with considerable asperity, accusing him of claiming to discover what Osann himself had discovered. To an impartial critic Osann wholly fails to make out his case. For nearly twenty years Claus continued his work, and his greatest service was in definitely settling the position of the six platinum metals among the elements (*Bull. Akad. St. Petersb.*, 1860 [2], ii., 160). He was the first who clearly showed that these six metals belong in a group by themselves. Up to this time many had held that platinum belonged with gold, palladium with silver, and ruthenium with tin.* He then arranges the elements in three pairs and in two series,† as we find them in every table to-day. He also speaks of ruthenium and osmium being especially close to iron, an analogy hardly acknowledged, even after the periodic tables of different chemists had appeared. He adds that while platinum is not in the group with gold, it is closely related to it.

Since the time of Claus no new metals have been found in platinum ore or belonging to the platinum group, which have been generally acknowledged as elements. Several chemists have, however, found what they have believed to be new elements, but the quantity has generally been so small that their verification has been impossible. In 1852 Genth (*Proc. Acad. Sci. Phil.*, 1852, vi., 209; *Amer. J. Sci.*, 1853 [2], xv., 446) found two grains of a white metal in platinum from California gold. Its properties were unlike those of any known element.

In 1862 Dr. C. F. Chandler (*Amer. J. Sci.*, 1862 [2], xxxii., 351) described a new metal in native platinum from Rogue River, Oregon. This possessed properties very similar to those described by Genth, and Chandler concludes that his metal is probably identical with that found by Genth.

In 1869 Guyard discovered a metal in Russian platinum which he described ten years later (*Monit. Scient.*, 1879 [3], ix., 795), and called uralium. It resembles platinum, but is softer, and has an atomic weight of 187.5. Its chief

difference from platinum is that when fused with potassium cyanide the melt is orange. This work of Guyard's has never been confirmed.

In 1877 Sergius Kern (*CHEM. NEWS*, 1877, xxxvi., 4, 92, 114, 155, 164; 1878, xxxvii., 65) announced the discovery of a new metal in platinum residues with atomic weight of 154, to which he gave the name of dayvum. This has not only not been confirmed, but recently Mallet (*Am. Chem. J.*, 1898, xx., 776) has gone over the whole ground with great care, and has shown that in all probability Kern's dayvum is a mixture of iridium with rhodium and a little iron. Mallet obtained a residue in much the same way as Kern with similar properties and atomic weight, but proved it to be a mixture. This is the more significant since 154 would be about the anticipated atomic weight of a metal lying between the lighter and heavier metals of the group.

The great influence of one of the metals of this group upon the properties of another, even if present in but small quantities, has already been alluded to. It has been long known, and a very considerable series of experiments on this point is described by Claus.* Nevertheless it remains true that a good proportion of the workers on these metals have for a time at least supposed themselves discoverers of new elements. We may say, however, that not yet is there any reliable evidence of any new metal between the two series, that is, with an atomic weight of about 150; nor has there been any trace of *ekamanganese*, with its atomic weight of 100, and which some chemists would expect to find resembling the platinum metals in its properties.

It is by no means impossible that new metals may be discovered in this group; but the fact that in more than half a century no confirmed discovery of such has taken place, and that had it not been for a misinterpretation of reactions by which ruthenium was overlooked, we might say that it lacked but three years of a century since a new metal has been discovered, is not calculated to give us much encouragement. There does indeed seem, according to the periodic table, to be a place for three metals of atomic weight near 150, but it hardly seems probable that such occur in any of the known platinum ores which have been so thoroughly investigated, unless it be in extremely minute quantity. There is, however, always the possibility of the discovery of new platinum ores, differing in character from those now known, which, whether from the Urals, or Colombia, or from the Pacific Coast, are approximately the same in composition.

We have seen that nearly half a century ago it was clear to Claus that iron, ruthenium, and osmium belonged in a group together. It was later easily recognised that cobalt, rhodium, and iridium furnished a second triad, while nickel, palladium, and platinum must also be grouped together. The analogies between the three metals of each of these groups is too patent to require discussion, though incidentally we shall have occasion to recur to it. When the elements were arranged in the first periodic tables, these metals did not fall into ordinary arrangement; as late as 1878 the atomic weight of osmium was considered greater than that of iridium, platinum, or even gold, while gold was given a weight less than that of iridium or platinum. Cobalt and nickel on one hand, and iridium and platinum on the other, were considered to have an identical atomic weight. The seeming impossibility of reconciling these nine metals with the periodic law is undoubtedly the reason why they were thrown out in a single group,—dumped into a chemical Gehenna as it were,—while the rest of the elements were reduced to orderly arrangement. Lothar Meyer, however, saw that there was a possibility that these elements also might be amenable to system, and under his direction Carl Seubert began the revision of the atomic weight of iridium

* *Loc. cit.* "Es ist nicht zu leugnen, das in Beziehung einiger weniger Eigenschaften sich solche Analogien aufstellen lassen, allein ich habe Grund diesen nur einen geringen Werth beizumessen, und schliesse mich daher entschieden dem ersten Theile der Anschauungsweise der Verfasser an, indem ich, wie ich mich auch bisher ausgesprochen habe, die Platinmetalle alle für Glieder einer untrennbaren, wohl begründeten Metallgruppe halte."

† + end of the horizontal series. { Principal Series. { Os. | Ir. | Pt. | Vertical Series. { - end of the horizontal series.
Secondary Series. { Ru. | Rh. | Pd. }

* C. Claus: "Beiträge zur Chemie der Platinmetalle," Dorpat, 1854, Chap. IV. "Modifikationen, welche die ursprünglichen Reactionen der einzelnen Platinmetalle durch Beimengungen der übrigen Metalle aus dieser Gruppe erfahren," p. 421.

("Inaug. Diss.," Tübingen, 1879). This he found to be more than four units less than the figure formerly used, and now the order of these elements appeared to be iridium, gold, platinum, osmium. Three years later Seubert (*Ber. d. Chem. Ges.*, 1881, xiv., 865) revised the atomic weight of platinum, finding it lower than that of gold, and this work was confirmed by Halberstadt (*Ber.*, 1884, xvii., 2962), and by Dittmar and McArthur (*J. Soc. Chem. Ind.*, 1887, vi., 799). The only anomaly in these four metals now was in osmium, and this also was resolved by Seubert (*Ber. d. Chem. Ges.*, 1888, xxi., 1839), who found that the old value of Berzelius and Frémy was about eight units too high, and that, so far from having an atomic weight greater than that of gold, osmium in reality has the lowest atomic weight of the four metals. This revision was justly accounted a great triumph for the periodic law.

As with the other metals, so also much doubt existed as to the atomic weights of rhodium and ruthenium; but the work of Seubert and of Joly, while changing somewhat the older figures, confirmed the order given in Meyer's table. Much work has been done on palladium by Keiser and by Keller and Smith in this country, by Bailey and Lamb and by Joly and Leidié abroad. The figures for platinum and palladium represent a much greater degree of accuracy than those for the other four platinum metals. Indeed it must be said that little accuracy can be claimed for the present figures of rhodium and iridium, and certainly those of ruthenium and osmium cannot be depended on more closely than half a unit.

In the case of the three other metals of this group, the atomic weight of iron has been well determined, but is now being subjected to a most careful examination in the laboratory of Professor Theodore Richards. As was supposed a few years ago to be the case with iridium and platinum, so cobalt and nickel were thought to have the same atomic weight. Then Lothar Meyer showed that, judged by their properties, nickel should follow cobalt in the periodic system, and hence have the higher atomic weight. Revisions of these metals followed, but the more accurate work the more probable it appeared that the atomic weight of nickel is below that of cobalt. It was suggested that nickel was quite possibly a mixture, and efforts were made to resolve it into its constituents. In this connection will be recalled the efforts of Gerhardt Krüss to decompose nickel, in which for some time he thought he had been successful, and christened the new metal gnomium. But like so many other aspirants for chemists' favour, gnomium proved to be but a mixture. The latest work on these metals, by Richards and Cushman and Baxter, far surpassing all that has previously been done, confirms the higher atomic weight of cobalt, and lends no support to the view that nickel is anything but a simple element.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

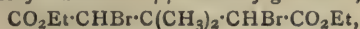
Ordinary Meeting, June 21st, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

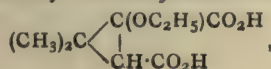
(Continued from p. 23).

96. "A New Series of Pentamethylene Derivatives." I. By W. H. PERKIN, jun., JOCELYN F. THORPE, and C. WALKER.

When ethyl $\alpha\alpha'$ -dibrom- $\beta\beta$ -dimethylglutarate,—

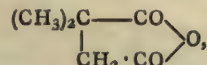


is treated with an alcoholic solution of potash, it is converted quantitatively into *ethoxycaronic acid*,—



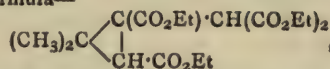
which separates from benzene in long needles melting at 136° ; the *anhydride*, made by distilling the acid, boils at 160 — 165° (50 m.m.), and on boiling with water is reconverted into the acid.

When warmed with concentrated sulphuric acid, or when heated with hydrobromic acid in a sealed tube, the acid is converted into the anhydride of *asym*-dimethylsuccinic acid,—

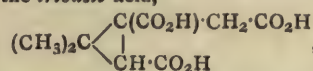


which melts at 39° , and on boiling with water yields *asym*-dimethylsuccinic acid melting at 139° .

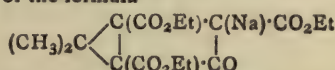
When ethyl dibromdimethylglutarate is condensed in alcohol solution with an equimolecular proportion of ethyl sodiomalonate, a 60 per cent yield of an ester of the probable formula—



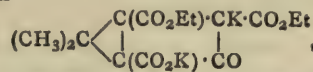
is produced; it is a thick liquid which boils at 234° (20 m.m.), and on hydrolysis with alcoholic potash is converted into the *tribasic acid*,—



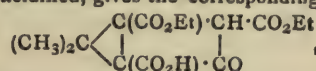
a colourless substance which separates from water in small needles and melts at 176° with evolution of aqueous vapour. When ethyl dibromdimethylglutarate is condensed with 2 equivalents of ethyl sodiomalonate in the presence of excess of sodium ethoxide, a yellow *sodium* compound of the formula—



is produced to the extent of 60 per cent of the theoretical amount; it is a remarkably stable substance, giving in alcoholic solution a deep red colouration with ferric chloride, and on hydrolysis in the cold with methyl alcoholic potash is converted into the yellow *potassium* compound—

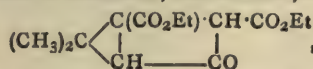


this, when acidified, gives the corresponding *acid ester*,—

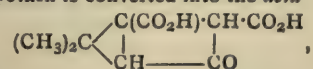


which crystallises from dilute alcohol in large prisms and melts at 75° .

On distilling this acid ester under diminished pressure, carbon dioxide is eliminated, and the *ester*,—

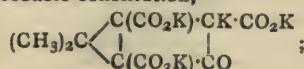


passes over at 201° (30 m.m.) as a thick oil which gives an intense violet colour with ferric chloride, and on hydrolysis with potash is converted into the *acid*—



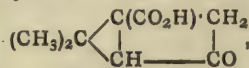
a colourless substance crystallising from concentrated hydrochloric acid in large prisms and melting at 179° ; it gives a red colouration with ferric chloride.

When the sodium compound mentioned above is treated with an equal weight of potash dissolved in ethyl alcohol, it passes into solution, and on boiling deposits a *potassium* salt, of the probable constitution,—



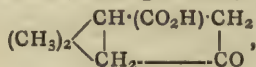
this, on being acidified, yields a mixture of two isomeric acids, which can be separated by re-crystallisation from dilute hydrochloric acid. The more soluble acid is identical with the acid mentioned above melting at 179°, the less soluble acid crystallises from dilute hydrochloric acid in needles melting at 154—155° with evolution of carbon dioxide; it gives an intense violet colour with ferric chloride; the first acid is called the α -, the second the β -modification.

Both modifications, the β on heating above its melting-point, the α on heating with water in a sealed tube at 200°, are quantitatively converted into the acid,—



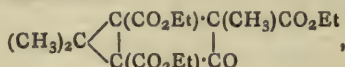
which crystallises from water in fern-like needles melting at 180° and subliming when heated, in long silky needles; the semicarbazone melts and decomposes at 225°, and the hydrazone at 217°.

On reducing the ketonic acid melting at 180° with sodium amalgam it behaves in a remarkable manner, the ketone group remaining intact and the trimethylene linkage being reduced, forming the acid,—



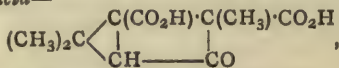
which separates from water in microscopic needles melting at 103°; the semicarbazone decomposes at 215°.

When the yellow sodium compound mentioned above is treated in alcoholic solution with methyl iodide it is converted into the ester—

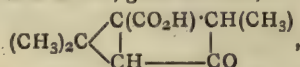


a colourless oil boiling at 219° (20 m.m.) and giving no colouration with ferric chloride.

On hydrolysis with methyl alcoholic potash, this ester is converted into a potassium salt which when acidified gives the acid—



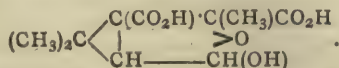
a colourless substance crystallising from benzene in lustrous plates melting at 146°; this, when heated in aqueous solution at 200°, gives the acid,—



which separates from water in glistening plates and melts at 134°; the semicarbazone decomposes at 230°.

If the potassium salt just mentioned be not separated, but the heating continued, it passes into solution with the formation of an acid characterised by being practically insoluble in dry ether, and which differs from the acid melting at 146° in containing 1 mol. of water of constitution. It separates slowly from water in large prisms melting at 237°, and when distilled under ordinary pressure passes over at about 270° as an oil which solidifies on cooling. This, on boiling with water, is converted into an isomeric acid which separates from water in needles melting at 180—181°, with formation of the anhydride.

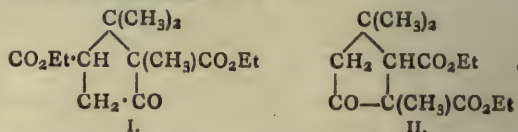
The reactions of these compounds seem to indicate that they are stereoisomeric furfuran derivatives having the formula—



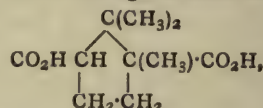
The investigation of these compounds, which are closely allied to several derivatives of the camphor and terpene series, is in progress, and experiments are being carried out in order to study the behaviour of other glutaric acids under the conditions indicated above,

97. "Experiments on the Synthesis of Camphoric Acid. III. The Action of Sodium and Methyl Iodide on Ethyl Dimethylbutanetricarboxylate." By W. H. PERKIN, jun., and JOCELYN FIELD THORPE.

When ethyl dimethylbutanetricarboxylate (*Trans*., 1899, lxxv., 900), dissolved in toluene, is treated with sodium and then with methyl iodide, a considerable yield of an ester is obtained which boils at 168—170° (18 m.m.), and on analysis gives numbers agreeing with the formula $C_{14}H_{22}O_5$. The method of formation of this substance clearly indicates that it must have one of the two following constitutional formulæ:—



If the ester has the constitution represented by Formula I., it must be closely allied to, and will probably be easily converted into, an acid having the constitutional formula—



assigned by Bredt to camphoric acid.

On reduction by means of sodium amalgam, this ester is converted quantitatively into a syrupy hydroxy-acid, which on long standing shows signs of crystallising. The analysis of this acid and its silver salt shows that it has the formula $C_{10}H_{16}O_5$; it is therefore isomeric with camphoric acid. The authors are continuing the investigation of these substances.

(To be continued).

NOTICES OF BOOKS.

Dictionary of the Bibliography of the Dyeing and Allied Industries. ("Dictionnaire méthodique de Bibliographie des Industries Tintoriales et des industries Annexes"). By JULES GARÇON. In three volumes. Vol. I. Paris: Gautier-Villars. 1900. Pp. 73.

This dictionary, or repertory, gives the titles of all papers, books, and documents published up to the end of the year 1896 which may be of interest to those engaged in the dyeing and allied industries.

Scientific and commercial work has increased of late years to such an extent as to have become international, and the technical papers published are so numerous that a special bibliography becomes indispensable for every industry.

Every subject bearing directly or indirectly on textile fabrics will be found in this repertory; it will therefore be of great use and assistance, not only to dyers, printers, and bleachers, &c., but also to all connected with textile fabrics or the chemical products used in their treatment.

The literature herein dealt with comprises about 2000 books and 110 periodicals; these latter consisting of 5000 volumes.

Electricity and its Applications. ("L'Électricité et ses Applications"). By Dr. FOUVEAU DE COURMELLES. Illustrated with 42 Figures in the text. Paris: Schleicher Frères. 1900. Pp. 185.

It is a far cry to the discovery of the electric battery by Volta, but the gigantic applications of electricity now in use all spring from that occurrence. Although in its applications electricity may to a certain extent replace steam power, it is very unlikely that the steam-engine

will be ousted from its unrivalled position as the prime motive power. Waterfalls are useful in a few places, but there are not many of them, and their use is limited to the neighbourhood in which they are situated. It is, however, in its diversity of application that electricity commands our attention; it gives us not only the electric tram, crane, and lift, but the telephone, electric bell, and telautograph, while in its later developments we get Röntgen rays and wireless telegraphy.

The present volume deals with the subject in a popular historical manner without going deeply into the mathematical side of the subject, and is well worth reading.

CORRESPONDENCE.

THERMAL CENTRES OF STABILITY.

To the Editor of the Chemical News.

SIR,—In the very interesting article on "The Existence of Thermal Centres of Stability in Compounds," by Mr. Geoffrey Martin, occurring in the CHEMICAL NEWS of June 29th, the author states that in endothermic compounds "the atoms are held together in such a way that energy is stored up in the molecule," and in the decomposition of such compounds "work is done *with*, not *against*, the internal atomic forces."

Now although this explanation may be quite clear mathematically, when one tries to interpret it physically it seems hardly comprehensible. If the resultant of all the internal atomic forces is such that the atoms within the molecule *repel* one another, how could they possibly have been made to combine?

In the case of ozone, an example of an "endothermic" compound, is it not more reasonable to suppose that it is formed *from its atoms* with the evolution of heat? If we conceive a number of free oxygen atoms in a vessel, there would then be two courses open to them, either to combine forming ozone molecules with the evolution of a little heat, or to combine forming oxygen molecules evolving a greater quantity of heat. Thus, starting with oxygen molecules, we cannot convert them to ozone molecules, except by supplying energy to the system.

The only alteration suggested in the theory would be the substitution of the term "minimum heat of formation" for "maximum negative heat of formation," and certainly "negative heat" is a difficult physical conception.—I am, &c.,

H. W. HILL.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

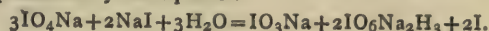
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. CXXX., No. 25, June 18, 1900.

Formation of Nitric Acid during the Combustion of Hydrogen.—M. Berthelot.—Experiments on the combustion of hydrogen have to be performed under very different conditions from those under which carbon and sulphur were burnt, owing to the fact that the combustion of these latter elements takes place only at their surface, whilst the gaseous oxygen and hydrogen mingle throughout their entire mass, and combustion is almost instantaneous. The author performs his experiments in two ways: (1) by burning a jet of hydrogen in an atmosphere of oxygen, the combustion taking place in a progressive manner and at constant pressure; or (2), by previously mixing the two gases and exploding the mixture in a closed vessel by an electric spark, the combustion taking place at constant volume.

Combustible Gases in the Atmosphere. Air of Towns.—Armand Gautier.—The author examined the combustible gases in the atmosphere, in the streets of Paris, in summer and in winter. His experiments show that formene appears to be, as was suspected, the hydrocarbon which exists in the atmosphere of towns. He also proves the existence, to a slight extent, of methane in the air, but always mixed with free hydrogen and other hydrocarbons richer in carbon.

Action of Oxidising Agents on Alkaline Iodides.—E. Péchard.—The author has already shown that periodate of sodium, IO_4Na , is an energetic oxidising agent, capable of reading on the alkaline iodides. He finds that a solution of this periodate decomposes sodium iodide in the cold. The solution thus obtained contains iodine, sodium iodate, and disodic periodate, the action being apparently represented by the equation—



This action is not instantaneous, the total quantity of iodine not being liberated until about an hour has passed. The next experiments were to find the action of ozone and hydrogen peroxide on potassium iodide. In each case analyses of the results were determined.

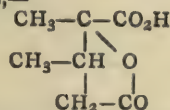
The Viscosity of Sulphur at Temperatures above the Temperature of Maximum Viscosity.—C. Malus.—Unsuitable for abstraction.

Selenides of Iron.—M. Fonze-Diacon.—The author prepares the compounds FeSe_2 , Fe_2Se_3 , Fe_3Se_4 , Fe_7Se_8 , and FeSe , corresponding to the sulphur derivatives of iron. He was unable to obtain the compound Fe_2Se by the reduction at a high temperature of iron selenides, this action only giving a mixture of iron and FeSe .

The True Atomic Weight of Boron.—G. Hinrichs.—M. Gautier has made two determinations of the atomic weight of boron from specimens prepared by M. Moissan. He finds that the ordinary atomic weight of boron is also the true weight. The application of the author's general method of calculation also bears out this statement, and proves that the specimen used must have been excessively pure. The atomic weight having 11.004 as a mean value, indicating that the true value should be exactly 11.

Action of Sulphurous and Hydrosulphuric Acids on Pyridine.—G. André.—In a former paper the author described a certain number of compounds of pyridine with formic, acetic, and propionic acids. He continues this research by considering the action of sulphur dioxide on pyridine, and was able—by direct combination of this gas with hydrogen sulphide, in presence either of pyridine alone or a mixture of water and pyridine—to prepare well-crystallised compounds, which are described.

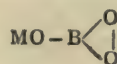
α - β -Dimethyl Glutolactonic Acids.—E. E. Blaise.—This preliminary notice relates to the α - β -dimethyl glutolactonic acids,—



which serves as the starting-point for the synthesis of the corresponding dimethylglutaric acids.

MISCELLANEOUS.

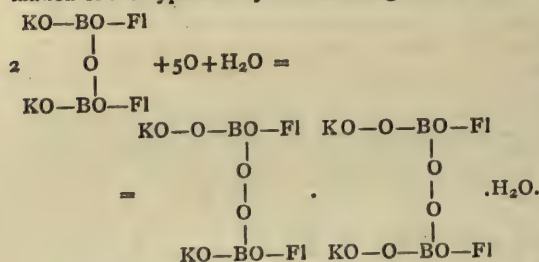
Fluohyperborates.—P. Melikoff and S. Lordkipan.—One of the writers has already published, in collaboration with M. Pissarjewsky, the results of a research carried out on the constitution of hyperboric acid, from which it follows that the salts of this acid may be given the general formula—



The experiments made, with a view to obtaining saline compounds corresponding with this formula, have not given very positive results. On the other hand, certain derivatives of hyperboric acid have the property of combining with the metallic superoxides. The authors used fluoroborate of potassium, $B_2O_3 \cdot 2KFI$, which they prepared by Schiff and Sistini's method, by melting a mixture of boric acid and fluoride of potassium. On treating this salt, under previously determined conditions, with peroxide of hydrogen and caustic potash, they obtained fluohyperborate of potash which crystallises in prisms belonging to the rhombic system, and which forms alkaline solutions with H_2O . These latter, submitted to the action of heat, give rise to an energetic disengagement of oxygen. By the action of dilute sulphuric acid they form H_2O_2 . With the dried salt, which is fairly stable, concentrated sulphuric acid causes the formation of ozonised oxygen.

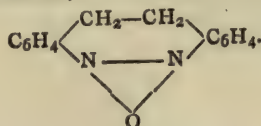
The relation between active oxygen, boron, and $\frac{K_2O}{2}$ in

the salt may be expressed by the figures 1:25:1:1. By dividing the active oxygen between the boron and the potassium, we can represent the constitution and the formation of the hyperacid by the following formula:—



The saline compound obtained represents the potassic salt of fluopyroboric acid, of which each H has been replaced by the radicle KO. The same substance may be prepared by acting with H_2O_2 on the potassic salt of orthofluoboric acid.—*Berichte*, vol. xxxii., p. 3349.

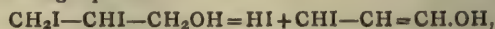
The Action of Sodium on Paranitrotoluene.—J. Schmidt.—By reading at the ordinary temperature with metallic sodium on paranitrotoluene, a still more energetic reaction takes place than with nitrobenzene, but in this case we do not obtain a hydroxylamine derivative. If, for example, we add one equivalent of sodium to ether containing one equivalent of paranitrotoluene in solution, we are able to isolate parazoxytoluene from the product of the reaction. Besides this compound a brown sodic substance is formed, insoluble in ether and inflammable in the air, and, according to the author, should be azoxydihydrostilbene,—



With two equivalents of sodium for one equivalent of paranitrotoluene there is produced, besides the above-mentioned brown sodic derivative, some parazotoluene and a small quantity of parazoxytoluene. The author proposes extending his research to other nitro and nitroso compounds, as well as to the oxides of nitrogen.—*Berichte*, vol. xxxii., p. 2919.

The Product of Decomposition of a Di-iodohydrine of Glycerin.—E. Charon and C. Paix-Séailles.—Di-iodohydrine of glycerin, $CH_2I-CHI-CH_2OH$, is easily prepared by dissolving iodine in slight excess of allylic alcohol. The mixture solidifies and crystallises easily. From this iodohydrine Hübner and Lellmann prepared a compound having formula C_3H_5IO , by loss of hydriodic acid, but they failed to determine the true nature of this

compound. The author's experiments lead him to believe that the di-iodohydrine decomposes according to the following equation:—



the substances formed being β -iodopropionaldehyde, the tautomeric vinylic form being unstable.—*Comptes Rendus*, cxxx., No. 24.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Oxide of Tin.—A correspondent in the United States asks for references to articles on the manufacture of oxide of tin.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2122.

THE EIGHTH GROUP OF THE PERIODIC SYSTEM AND SOME OF ITS PROBLEMS.*

By JAS. LEWIS HOWE.

(Continued from p. 33).

HERE we meet apparently one of those chemical mysteries which seem to baffle our attempts at solution. We are not permitted to doubt the correctness of the general principles of the periodic system, and yet here—and the case is perhaps not unique—two elements seem to have exchanged places. When we know *why* the properties of an element are a function of its atomic weight, we shall perhaps come to understand why the atomic weight of nickel is not greater than that of cobalt.

If the chemical study of these metals all supports the conception of their elementary nature, an examination of the spectrum of nickel and of cobalt, and particularly of iron, forces upon us the thought of the complexity of the atom. If each line of the spectrum, representing the vibration of a certain wave-length, is occasioned by a corresponding vibration of the atom, it becomes difficult for us to conceive of so many hundred simultaneous vibrations of a simple atom, a great share of which stand in no apparent harmonic relation to each other. It has been suggested that it is by a study of the spectroscopic portrayal of atomic vibration we may hope to gain the most complete knowledge of the dynamical character of the atom; but it must be remembered that with the spectroscope we study the motion of the atom at a high temperature, where vibration apparently overcomes in most instances chemical affinity; a knowledge of the atom at this temperature may give us no hint whatever as to the nature of the atom at lower temperatures, even as the spectrum of the same element may change with varying temperature. While we might thus conjecture that perhaps by some process of careful and refined fractionation, it might be possible to resolve iron into a series of meta-elements with nearly the same atomic weight, we are met by the fact that, complex though it is, we find not only the same spectrum for iron, whatever its terrestrial source, but that the spectrum of sideral iron, from meteorite, from sun, from star, gives us no evidence of any variation in the composition of iron. We are, I think, justified in concluding that the nine metals of the eighth group fulfil every definition of an element, and that they are just as much to be looked upon as simple elementary substances as any of those substances which we call elements; and further, that while refined determinations may change, to a slight extent, the atomic weight of some of these elements, especially those of ruthenium and osmium, we may expect the weight of these elements relative to each other, and hence their position in the periodic system, to remain unchanged. This, of course, carries with it the conclusion that in the periodic table an element may have an atomic weight slightly lower than that of the element which precedes it. I have discussed this possibility briefly elsewhere (CHEM. NEWS, 1899, lxxx., 74), and will only add that seeming exceptions to accepted laws, instead of overthrowing the law, often serve to broaden our conception of the law itself.

Before considering some of the compounds of the metals of the eighth group, attention must be called to

the phenomenon exhibited by several of these metals, and particularly by palladium, of condensing hydrogen and other gases upon their surface. The first observation in this connection seems to have been that of Sir Humphry Davy (*Phil. Trans.*, 1817, cvii., 77), who, in 1817, showed the Royal Society how a warm platinum wire, plunged into the vapour of alcohol or ether, or certain other inflammable gases, became incandescent, and continued to glow as long as kept in the vapour, causing an oxidation of the gas, and in some mixtures even an explosion. This phenomenon attracted great attention on the part of chemists, and many were the discussions over this lamp "without a flame," or Davy's "aphlogistic lamp" as it was called. It was soon after noticed by Edmund Davy (*Phil. Trans.*, 1820, cx., 108) that the platinum reduced from solution, now called platinum black, but then platinum suboxide, is especially active, and can oxidise alcohol to acetic acid. In 1823 Döbereiner announced (*Schweigger, J. für Chem.*, 1823, xxxviii., 321) that platinum black and platinum sponge, when held in a stream of hydrogen, ignite the gas, and that the hydrogen is absorbed by the platinum. This was the origin of Döbereiner's hydrogen lamp, regarding which he writes, under date of Aug. 5, 1823:—"You have doubtless guessed before this that I have already utilised this new observation (of the heating effect of the condensation of hydrogen) for the preparation of a new Feuerzeug and a new lamp, and that I shall put it to many other important uses" (*J. für Chem.*, loc. cit.). The interest which attached to this discovery of Döbereiner's can be judged by the fact that in the literature of the decade following are found over fifty references to the subject. Little attention was, however, paid to the similar action of palladium upon combustible gases, although the phenomenon had been noticed, until in 1868, half a century subsequent to Davy's first observation on platinum, Graham presented to the Royal Society his remarkable paper on the occlusion of hydrogen by metals (*Proc. Roy. Soc.*, 1868, xvi., 422), followed the next year by his papers on the relation of hydrogen to palladium (*Proc. Roy. Soc.*, 1869, xvii., 212), and additional observations on hydrogenium (*Proc. Roy. Soc.*, 1869, xvii., 300).

Graham's view that the hydrogen is present in solid form as a metal, and that the palladium saturated with hydrogen must be looked upon as an alloy, was received with considerable dissent. The work of Troost and Hautefeuille (*Comptes Rend.*, 1874, lxxviii., 686, 968; and 1875, lxxx., 788) tended to the view that the substance is a definite compound, Pd₂H. Against this is the fact that the conductivity of palladium is but slightly reduced by the occlusion of hydrogen. Calculations of the specific gravity of Graham's hydrogenium by Dewar gave the number 0.62, and the same figure is obtained for the hydrogen in hydrides of sodium and potassium, studied by Troost and Hautefeuille. The recent determinations of the specific gravity of liquid hydrogen by Dewar, however, show a figure only about one-ninth of the density of occluded hydrogen, so that the question as to the nature of the hydrogen condensed by the palladium and platinum remains still unsettled. The other metals of the group possess this property to some considerable degree, but much less than is the case with palladium and platinum. In this connection it is interesting to note that one of the earliest papers of Dewar was on the motion of a palladium plate, during the formation of Graham's hydrogenium (*Proc. Roy. Soc. Edinb.*, 1869, vi., 504).

Reference has been made to the natural grouping of the elements of the eighth group into three triplets, iron, ruthenium, osmium; cobalt, rhodium, iridium; and nickel, palladium, platinum. That this is a natural grouping is attested by a comparison of the compounds of these metals. However, in considering now some of these compounds, the evidence of this grouping is only incidentally presented; I desire chiefly to call attention to some of the more unusual of these compounds, especially with reference to problems which this group pre-

* An Address delivered before the American Association for the Advancement of Science, New York Meeting (1900), Section C.

sents, and to problems of other groups, suggested by the chemistry of this group.

The position of an element in the periodic system is, to a very considerable extent, determined by its oxides, and that too by its highest oxides, excluding the peroxides of the hydrogen peroxide type; a considerable number of these last have been studied especially by Melikoff and Pissarjewsky of Odessa; but their character still presents many points of obscurity, and cannot be used with reference to the periodic law. The triplet iron, ruthenium, osmium, presents the highest oxides of the eighth group, and, as is the case with other divisions of this group, an increasing stability of the higher oxides with increasing molecular weight. The type of salts of the acid-forming oxides FeO_3 , RuO_3 , OsO_3 , occurs in this group, as in the positive series of the elements of the sixth and seventh groups; viz., CrO_3 , MnO_3 , WO_3 , UO_3 , MnO_3 . This type is not represented in the second or third triplet of group eight. Potassium ferrate, K_2FeO_4 , exists only in solution and is very unstable; potassium ruthenate, K_2RuO_4 , is stable when dry, but slowly decomposes when in solution; potassium osmate, K_2OsO_4 , on the other hand, has a very considerable degree of stability. Of the lower base-forming oxides, iron has not only the sesquioxide, Fe_2O_3 , and monoxide, FeO , but also several intermediate oxides, which may be looked upon as merely compounds of these two—such is magnetite. In the case of ruthenium, the sesquioxide, Ru_2O_3 , seems to be what one might call the normal base-forming oxide. The different conditions which occasion the formation of the lower oxides of osmium are ill known, though several different oxides seem to exist, as OsO , Os_2O_3 , and OsO_2 . Much more interest, however, attaches to the tetroxides of ruthenium and of osmium, RuO_4 and OsO_4 , which are the highest volatile oxides of any known element. The almost intolerable odour of osmium tetroxide incited Tennant, in 1803, to give its name to this element, while ruthenium tetroxide, first noticed by Claus, has, if not too concentrated, a rather fresh pleasant odour, with just a suspicion of the smell of ozone, due probably to the formation of ozone in the decomposition of the oxide. As far as physical properties go, these oxides, while solid at ordinary temperature, melt easily and can be distilled. Ruthenium tetroxide is, however, far less stable than the corresponding osmium oxide, for it decomposes slowly at ordinary temperature, and explodes with great violence if heated much above 105° . On one occasion Deville and Debray (*Ann. Chim. Phys.*, 1875, [5], iv. 537) attempted to distil 150 grms. of ruthenium tetroxide, and, when the temperature reached a little above 100° , the whole mass exploded with terrific violence, filling the laboratory with a dense sooty smoke. In a recent similar explosion in my own laboratory, occasioned by the contact of a little alcohol with ruthenium tetroxide, but happily on a much smaller scale than that of Deville and Debray, this black soot was found to be readily soluble in hydrochloric acid. This is unexpected, as all the anhydrous lower oxides of ruthenium are insoluble in acids, and from its method of formation the black substance could hardly be anything other than an anhydrous oxide or the metal itself. Osmium tetroxide is commonly known as osmic acid; but as a fact these tetroxides are neither acid-forming oxides nor are they peroxides in the ordinary acceptance of the term. When treated with an alkali we have a gradual reduction with formation of perruthenate and ruthenate, or of osmate.

Turning to the third triplet, we have the monoxide of nickel well characterised, and it is, we may say, the only well-characterised oxide of the metal, for though higher hydrated oxides of nickel exist, and perhaps anhydrous oxides also, their composition is not definitely known. With palladium and platinum also monoxides seem to exist and dioxides as well (PdO_2 and PtO_2). Platinum dioxide may be looked upon as being perhaps a very weak acid-forming acid. While nickel forms practically only the monoxide, NiO , and iron forms from choice, as we

might say, the sesquioxide, Fe_2O_3 , the intermediate metal cobalt, while forming most generally the monoxide, is easily oxidised to the sesquioxide, Co_2O_3 , and thus cobalt may be considered in its relations to oxygen as intermediate between nickel and iron. Similarly in the case of rhodium and iridium, there is a strong tendency to form the sesquioxide, so that this middle triplet is intermediate between the other two triplets of the group. As a whole, there is a large field at hand in a revision of the oxides of this group, especially those of the first triplet.

The same may be said even more emphatically of the sulphides. Those of iron, cobalt, and nickel are fairly well investigated, but of the remainder comparatively little is known except the somewhat exhaustive work of Schneider on the thioplatinates and thiopalladates. After a very considerable amount of work upon the sulphides of ruthenium, I have come to distrust about all that has been published, and to have nothing definite to add myself. The precipitates with hydrogen sulphide from ruthenium solutions (RuCl_3) contain apparently considerable free sulphur, but oxidise very rapidly with formation of sulphuric acid on drying, making their composition very difficult of determination. From ruthenate solutions a sulphide is precipitated which seems to have the formula RuS_3 , but there is no assurance that a part of the sulphur may not be free and not combined.

Of all the compounds of the metals of the eighth group, by far the best investigated are those with the halogens, and upon our knowledge of these rests the greater part of our chemical knowledge of the platinum metals. Yet here again our knowledge is wholly inadequate. If we except the work done under Wöhler's direction, by Oppler and Birnbaum on the bromides and iodides of iridium, that by Topsøe on the bromides and iodides of platinum, we may say that very little is known of any haloids of this group except the chlorides. In some instances, as with ruthenium, even the chlorides are very unsatisfactorily known. Of nickel we know only the bichloride NiCl_2 ; of cobalt the only stable chloride is the bichloride, CoCl_2 ; but the trichloride, CoCl_3 , seems capable of existence in solution; of iron, the ferric chloride, FeCl_3 , is the stable compound, into which the ferrous chloride, FeCl_2 , is readily oxidised. Here again the intermediate position of cobalt is apparent. There is a strong tendency on the part of all these chlorides to form double salts, of which we have examples in $\text{K}_2\text{FeCl}_4 \cdot 3\text{H}_2\text{O}$, K_2FeCl_5 , and Rb_2FeCl_6 . These salts seem to be broken up in solution, and the chlorine can be precipitated by silver nitrate. Turning to the halogen compounds of the platinum metals, we find double salts of a very different character. The common types for platinum and palladium, for example, are K_2PtCl_4 and K_2PtCl_6 . This latter type seems also to be known for all platinum metals except rhodium. Osmium, iridium, and rhodium present also the type K_3OsCl_6 , while ruthenium and rhodium also form salts of the type K_2RhCl_5 . The most important feature of these salts is that they are not decomposed when dissolved in water, silver nitrate precipitating not silver chloride alone, but the double chloride of the metal and silver; that is, for example, when K_2PtCl_6 is dissolved in water it is electrolytically dissociated, K being the positive ion, while the negative ion is the group PtCl_6 . The platinum metal then in these salts is a part of the negative ion. Double salts of this class are, of course, well known, but nowhere are they developed to the same extent as in the eighth group, indeed double salts of several acids are found among no other metals. The question may be fairly raised among the platinum metals as to whether there is any salt which is electrolytically dissociated giving the platinum metal as the positive ion.

The chlorides of ruthenium furnish an instructive illustration of the difficulties which may arise in getting complete knowledge of chemical facts as to what would naturally be considered simple substances. As we have seen, Claus discovered ruthenium in 1844. He obtained two chlorides or rather double chlorides, the one K_2RuCl_5 ,

and the other K_2RuCl_6 , the former corresponding to the type found in osmium and rhodium, the latter that found in platinum and palladium as well as iridium and osmium. In describing this latter salt, Claus shows that it was in the hands of Berzelius and probably in a pretty pure state, but that that chemist thought it to be an iridium salt. Berzelius was not convinced, and in the "Handwörterbuch der reinen und angewandten Chemie," edited by Liebig, Poggendorff, and Wöhler, the work of both Berzelius and Claus is given. This was naturally somewhat irritating to Claus, and he writes (*Bull. Akad. St. Petersb.*, 1860, [ii.], i., 108), "Even if reverence for the great authority of the great chemist (Berzelius) should seem to justify such a course, regard for the truth of science should not have permitted it." The subject was now dropped, and for a third of a century no one had worked upon this chloride, when Professor A. Joly, of the *l'Ecole Normale*, began his study of the platinum metals, and much of the work of Claus upon ruthenium was revised. Now it appeared that not only Berzelius, but also Claus himself was mistaken, and what he had taken for a chlor-ruthenate, K_2RuCl_6 , was in reality a nitroso-chlor-ruthenate, K_2RuCl_5NO . My own work of a little later date upon the chlorides of ruthenium abundantly confirmed this. Many efforts were made to prepare a tetrachloride of ruthenium, but it proved elusive. It may be noted in this connection that the cesium and rubidium nitrosochlorides exist in an anhydrous as well as in a hydrated form, and while the very easily soluble hydrated salts lose their water on warming the solution, the very slightly soluble anhydrous salt being precipitated, the reverse change is seemingly impossible, as the anhydrous salt will not take up water and pass back into the hydrated form.

The history of the higher chloride of ruthenium is not yet completed. Within the past year Professor Ubaldo Antony and A. Lucchesi, of the University of Pisa, have described (*Gazz. Chim. Ital.*, 1899, xxix.) the preparation of the real tetrachloride, K_2RuCl_6 , which, like the corresponding salts of platinum and the other metals of the group, crystallises in octahedra. I have more recently, by methods similar to those of Antony, prepared the cesium salt, Cs_2RuCl_6 , which also crystallises in octahedra and corresponds to Antony's salt; and I have also been fortunate enough to obtain a new salt of a rare type, lying intermediate between the tetroxide and the tetrachloride, $Cs_2RuO_4Cl_4(2CsCl, RuO_2Cl_2)$. Now a question may arise here as to whether Claus was, after all, wrong in believing he had the tetrachloride. As the salt was commonly made by Claus, by the action of nitric acid, it was, without question, a nitrosochloride, and his description corresponds completely; but Claus adds in a foot-note (*Z. Prakt. Chem.*, 1846, xxxix., i., 96) that it is also possible to prepare the salt by heating the trichloride with potassium chlorate and hydrochloric acid. This could not give the nitrosochloride, but while under these conditions the tetroxide is usually formed, it is possible that the tetrachloride may also have been formed. In another place he speaks of making it by the action of hydrochloric acid on potassium ruthenate, but in the presence of saltpetre. Except for this latter salt, this is the method of Antony, but usually at least it gives the trichloride. The salt which Claus generally describes is the nitrosochloride, but in one place (*Bull. Akad. St. Petersb.*, 1860, [ii.], i., 105) he says the salt seems to be dimorphous, for after crystallising out the common prismatic crystals (of the nitrosochloride) he, on one occasion, obtained large regular octahedra, isomorphous with tetrachlorides of the other platinum metals. As the molecular weight of the nitrosochloride is almost the same as that of the tetrachloride, and as the chlorine seems to have been generally estimated by loss, analysis would reveal no discrepancy, but in one case, at least, the chlorine was directly determined, and these figures can be accounted for only on the supposition that in this case it was a tetrachloride which was analysed, so that it would seem possible that Claus

actually formed the tetrachloride, although he did not distinguish it from the nitrosochloride. Even now the conditions of formation of the tetrachloride are obscure, and not less so is the cause of a phenomenon, noticed first by Claus, and since his day used as a test for the detection of ruthenium, and which is familiar to all of you who have experimented at all with this metal. I refer to the beautiful indigo-blue colour assumed by the solutions of ruthenium trichloride when hydrogen sulphide is led into them. Since, at the same time, sulphur is precipitated, and since the trichloride assumes a blue colour on treatment also with metallic zinc,* it was assumed by Claus that reduction has taken place, and hence that the solution contains ruthenium bichloride, $RuCl_2$. When ruthenium is heated in a current of mixed chlorine and carbon monoxide, it increases many times in volume, and there is formed an anhydrous trichloride. This is insoluble in water and in strong alcohol, but dissolves with considerable readiness in dilute alcohol to a similar deep blue solution. Joly succeeded in distilling off the alcohol and water from this solution, in a vacuum, and obtained a blue deliquescent substance which he considered to be an oxychloride, $RuOHCl_2$. I have also formed this blue solution by electrolytic action, and while it seems to be formed by a reducing action this is not perfectly clear.

Considerable work upon this solution, however, leads me to agree with Claus that it is probably a lower chloride of ruthenium, but it has not been proved. I have dwelt perhaps unduly upon these compounds, for the purpose of showing the obscurity in which even such seemingly simple points are enveloped, for it well illustrates how much work must yet be done before we acquire any adequate knowledge of the nature of even the commoner compounds and reactions of these elements.

(To be continued).

THE DISTRIBUTION OF MOLECULAR ENERGY.†

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University of Cambridge.

THIS Paper attempts to examine the well-known difficulties in connection with the partition of energy in the molecules of a gas. A definite dynamical system is first considered, an ideal gas in which the molecules are loaded spheres, that is spheres of radius a , of which the centre of mass is at a small distance, r , from the geometrical centre. It is shown by direct methods that the energy will, after an infinite time, distribute itself equally between the five degrees of freedom; but when a wave of sound is passed through the gas, the energy will never have sufficient time to attain to its equilibrium distribution. It is shown that sounds of different period will be propagated with appreciably different velocities, except in the extreme case in which the ratio of r to a is almost, but not necessarily quite, zero. In this case the ratio of the two specific heats, as determined from indirect experiments on the velocity of sound, would be $\frac{13}{12}$, while direct experiments might give any value from $\frac{13}{12}$ to $\frac{13}{12}$, the value varying with the duration of the experiment.

It is suggested that an escape from this dilemma is made possible by regarding the molecules as forming an incomplete dynamical system, of which the ether is the remaining part. For purposes of illustration, it is imagined that the interaction between the two parts of this complete system consists of a frictional force which retards the rotation of the molecules. A steady state is

* It has already been mentioned that Vauquelin had noticed this blue colour, but not knowing of ruthenium had attributed it to osmium.

† Abstract of a Paper read before the Royal Society, June 21, 1900.

now impossible, but it is shown that when the energy (i. e., temperature) of the gas is sufficiently low, the gas tends to assume an approximately steady state, in which the energy of rotation vanishes in comparison with that of translation.

It is then shown that these conclusions may be generalised so as to apply to a more complex system of molecules, these molecules possessing an indefinite number of degrees of freedom, and internal potential energy as well as kinetic. The molecules exert forces on one another at any distance, and the radiation is of a more general type than before.

In Part III. some of the physical consequences of the view here put forward are examined. The final conclusions are briefly as follows:—

The degrees of freedom must be weighted, not counted. The weight of a degree of freedom may be anything between unity and zero, and may vary with the temperature. A degree of freedom which does not radiate energy will always be of weight unity; for a non-luminous gas, one which does radiate energy when the gas is heated, is of weight zero.

As the gas is heated, the radiation and internal energies will increase much more rapidly than the temperature, until finally, at infinite temperature, the energy is distributed equally between all degrees of freedom.

Finally it is pointed out that this view is in accordance with ordinary thermodynamics for a non-luminous gas, but that the ordinary thermodynamics must be supposed to break down above the temperature of incandescence, a view which has already been put forward, in a modified form, by Wiedemann.

ANALYSIS OF THE NATURAL MINERAL WATER FROM THE No. 3 SPRING, BRAULT, SAIL-SOUS-COUZAN (LOIRE).

By EDMOND BONJEAN.

This water is particularly interesting by reason of the large amount of carbonic acid which it contains, and by its mineral richness, which causes it to be of the most mineralised type and of the greatest purity of any water in this hydro-mineral region.

The flow of this spring, measured by M. Coste, a well-known mining engineer, on February 17th, 1900, was 51 litres per minute: its invariable temperature is 12°.

The analyses were made on samples taken by me on August 27th, 1898.

The results are expressed in grms. per litre:—

I. Elementary Analysis.

	Grms.
Total carbonic acid	4.387
Combined carbonic acid	1.561
Free carbonic acid (1438 c.c.)	2.826
Silica, as SiO ₂	0.027
Oxide of iron, as Fe ₂ O ₃	0.011
Oxide of manganese	distinct traces
Lime, as CaO	0.126
Magnesia, as MgO	0.0997
Soda, as Na ₂ O	0.8205
Potash, as K ₂ O	0.1425
Lithia, as Li ₂ O	0.0025
Arsenic, as As	0.0005
Sulphuric acid, as SO ₃	0.0185
Chlorine, as Cl	0.0577
Ammonia and ammoniacal salts	traces
Organic matter	traces
Nitrates, nitrites, phosphoric acid, strontium	none
Residue at 110–120°	2.1305
Alkalinity in CO ₃ Na ₂	1.990

II. Combination of the Fixed Elements.

	Grms.
Silica, as SiO ₂	0.027
Ferrous carbonate, CO ₃ Fe	0.016
Carbonate of lime, CO ₃ Ca	0.225
" magnesia, CO ₃ Mg	0.2093
" lithia, CO ₃ Li ₂	0.0062
" soda, CO ₃ Na ₂	1.2918
" potash, CO ₃ K ₂	0.2098
Sulphate of soda, SO ₄ Na ₂	0.033
Chloride of sodium, NaCl	0.095
Arsenate of sodium, AsO ₄ Na ₃	0.0014
	2.1145

III. Probable Combination of the Elements in Solution.

	Grms.
Free carbonic acid (1438 c.c.)	2.826
Silica, as SiO ₂	0.027
Ferrous bicarbonate, FeCO ₃ .CO ₂	0.022
Bicarbonate of manganese	distinct traces
" lime, CaCO ₃ .CO ₂	0.3240
" magnesia, MgCO ₃ .CO ₂	0.3180
" soda, NaHCO ₃	2.0462
" potash, KHCO ₃	0.3032
" lithia, LiHCO ₃	0.0099
Sulphate of soda, SO ₄ Na ₂	0.0330
Chloride of sodium, NaCl	0.0950
Arsenate of sodium, AsO ₄ Na ₃	0.0014
Ammonia and ammoniacal salts	traces
Organic matter	traces
Total elements in solution	6.0057

Bacteriological Examination.—Cultivations conducted on the spot enable me to affirm that this water is sterile. —*Bull. Soc. Chim.*, Ser. 3, xxiii, No. 10.

ON ELECTRIC TOUCH AND THE MOLECULAR CHANGES PRODUCED IN MATTER BY ELECTRIC WAVES.*

By JAGADIS CHUNDER BOSE, M.A., D.Sc.,
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(Note added March, 1900.—In the various investigations on the properties of electric waves, one property has not yet attracted so much attention as it deserves—the action of long ether waves in modifying the molecular structure of matter. Apart from the interest attached to the relation between ether, electricity, and matter, the subject is of importance as affording not only a very important verification of the identity of visible and electric radiation, but also establishing the continuity of all radiation phenomena. These phenomena occupy the borderland between physics and chemistry, and their study may therefore be expected to throw much light on several subjects at present imperfectly understood. The study of the action of electricity and of ether waves on matter in the form of solids presents many difficulties, owing to the great complexity of atomic and molecular aggregation which characterises the solid state of matter. But the phenomena often met with in theory and practice is, unfortunately, in reference to matter in a solid state. The means of investigation are almost wanting: chemical tests give us no information, for they tell us (and that in a few cases only) of the ultimate change in the mass as a whole, and not of the protean transformations that are constantly taking place in it under the action of ever-varying changes in physical environments. In the following investigations the difficulties mentioned above were constantly present, and the attempts to meet them may therefore be of some interest.)

* A Paper read before the Royal Society, February 8, 1900.

In my former paper ("On a Self-recovering Coherer, and the Study of the Cohering Action of Different Metals," *Proc. Roy. Soc.*, vol. lxxv.), I described the contact-sensitiveness of various elementary substances to electric radiation. It was shown that though many substances exhibit a diminution of contact-resistance, there are others which show an increase of resistance—an increase which, in certain cases, lasts only during the impact of electric waves, the sensitive substance automatically recovering its original conductivity on the cessation of radiation. There are thus produced two opposite effects, either an increase or a diminution of resistance, depending on the nature of the substance.

The effect of increase of contact-resistance is not an exceptional or isolated phenomenon, but is as normal and definite under varied conditions as the diminution of resistance noticed in the case of iron filings. These two specifically different effects have to be recognised, and it would be advisable, to avoid misunderstanding, to use a simple term to indicate both these effects, and distinguish them from one another, by calling the one positive and the other negative. The term "coherence" applied to the normal diminution of resistance exhibited by certain metals by the action of electric waves cannot be applied in all cases, as there is, as has been said before, another class of substances which exhibits under normal conditions an increase of resistance. The term "decoherence" has been used to indicate the effect of mechanical tapping on fatigued substances of the former class; this produces an increase of resistance, and at the same time restores the sensitiveness. The action of tapping on fatigued specimens of the latter class is, however, a diminution of resistance.

I have shown in a former paper that the seat of sensitiveness is confined mainly to the surface layer of the sensitive substance, and that the nature of the substratum has little or no effect on the sensitiveness. Thus, a substance which exhibits a strong diminution of resistance, if coated with an extremely thin layer of a substance of the other class which shows an increase of resistance, will now exhibit an increase of resistance. It is seen that the action is one of the bounding layer or skin of the sensitive substance. There is a Sanskrit word, *twach*, which means the skin; and as the phenomenon dealt with in the present paper is one of sensitiveness of *twach*, I shall use the expression "electric touch" in the restricted sense of contact sensitiveness to electric stimulus, the touch being regarded as *positive* when electric oscillation produces an increase of conductivity or diminution of resistance, and *negative* when the contrary effect is produced. Substances which exhibit a decrease of resistance will be called positive, and those which show an increase will be regarded as negative. The above terms are to be regarded as convenient substitutes for long descriptive phrases.

The phenomenon of contact-sensitiveness seems at first to be extremely anomalous, and there appears to be little relation between substances which exhibit similar electric sensitiveness. Taking iron as an example of a very sensitive substance, it is seen to be easily oxidised, and from this it may be inferred that a slight oxidation on the surface is favourable for sensitiveness. This view obtains some support from the consideration that the so-called noble metals are not as sensitive as iron. But the metals nickel and cobalt, which are bright and not easily oxidised, are also very sensitive. The very sensitive metals iron, nickel, and cobalt are all magnetic, and it might be thought that magnetic property is favourable for electric sensitiveness, but a dial magnetic substance like bismuth is also found to exhibit a fairly strong sensitiveness. Again, from the strong diminution of resistance exhibited by magnesium, it may be inferred that the sensitiveness depends on the electro-positive character of the metal; but potassium, one of the most electro-positive metals, exhibits an unusual increase of resistance, a property which it will be shown in a future paper it shares with some of the most electro-negative elements.

There is one property, however, which at first would seem to be in some way related to the sensitiveness of metals—the volatility of metals under the cathodic stimulus, investigated by Sir William Crookes (*Proc. Roy. Soc.*, vol. l.), who gives the following list of metals, arranged according to their volatility:—

Palladium	108
Gold	100
Silver	80.68
Lead	75.04
Tin	56.96
Brass	51.58
Platinum	44
Copper	40
Cadmium	31.99
Nickel	10.99
Indium	10.49
Iron	5.5
Magnesium	} very
Aluminium	} slight

In this list the substances which are most volatile, e.g., Pd, Au, Ag, are not very sensitive, whereas Fe, Al, Mg, which are least volatile, are strongly sensitive. But the above series does not exactly coincide with the series of electric sensitiveness. Again, the volatility of platinum is retarded in hydrogen gas, but an experiment carried out to determine the sensitiveness of platinum in hydrogen failed to show any great increase in the sensitiveness.

None of the above suppositions give any satisfactory explanation of the numerous anomalies in the contact-sensitiveness of metals. It then appeared that the observed effect is not due to a single cause but to many causes. An observer studying the dilatation of a gas under reduced pressure, and ignorant of the effect of temperature, will doubtless encounter many anomalies. In the phenomena of contact-sensitiveness the variables are, however, far more numerous, and the different possible combinations are practically unlimited. It therefore became necessary, by a long and tedious process of successive elimination, to find out the causes which are instrumental in producing the observed effect; the results obtained throw some light on this intricate subject. The following are some of the principal directions in which a systematic inquiry was carried out:—

- On the difference between mass action and molecular or atomic action, with reference to the phenomenon of contact-sensitiveness.
- On the change of sign of response in a receiver due to a variation of the radiation intensity.
- On the physico-chemical changes produced in a sensitive substance by the action of electric radiation, and on the radiation-product.
- The phenomena of electric reversal and of radio-molecular oscillation.
- On "fatigue" and the action of mechanical tapping and other disturbances by which the sensitiveness of a fatigued receiver may be restored.
- On the nature of the passage of electricity through imperfect contacts, and the influence of various physical agents on the current.
- On the systematic study of the contact-sensitiveness exhibited by metals, non-metals, and metalloids.
- On the contact-sensitiveness exhibited by alloys and compounds.

I intend to treat the above subjects in some detail, and in the present paper will especially deal with the first five lines of investigation. These, it is hoped, will afford an explanation of some of the most perplexing anomalies. All the subjects mentioned above are more or less interdependent, but their treatment in one paper would make the subject very complicated. It would be easier to take a more generalised and complete view of the subject as a whole, after each of the above-mentioned inquiries has been separately considered. With reference to the flow

of electricity through imperfect contacts, I need only mention here that the phenomenon seldom obeys Ohm's law. In many instances the phenomenon appears more allied to the discharge of electricity through a gaseous medium.

(To be continued).

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART III.

By HARRY BREARLEY.

(Concluded from p. 27).

CARBON (continued).

IV. COLORIMETRIC ESTIMATION OF CARBON.

IV.a. Eggertz Process and Modifications.—

429. EGGERTZ (C. N., xlv., 173).—Desirable relation between C in steel, HNO_3 , and state of dilution. Daylight bleaches colour. Comparison made in camera. Likely amounts of Mn, P, Si (see 444), S (see 434), W, Cr (see 435), Va, Ni, Co, and Cu are without influence. Permanent artificial standards. (See also 372).
430. HERMANN (C. N., xxi., 295).—Artificial standards not satisfactory. Process not suitable for high carbon steels.
431. GREINER (C. N., xx., 286).—The nitric solution of the steel is kept for four hours at 80° before comparing with the standard.
432. ROSSI (Y. I. S. I., 1891, i., 433).—Samples dissolved at $80-85^\circ$ C., and the colours compared in a Duboscq colorimeter, which is described.
433. BRITTON (C. N., xxvi., 139).—Use 1 grm. of material; dissolve without heat, filter, and compare with series of standards (coffee in alcohol). Sample loses colour on standing.
434. HOGG (C. N., lviii., 175).—The S of a sample is liberated as such, and has a very marked influence on the tints.
435. ZIEGLER (Y. I. S. I., 1890, i., 373).—Chromium gives a grey tone to Eggertz colour solution.
436. TROILIUS (C. N., xlv., 292).—Compares between two standards not differing much in percentage from the sample.
437. SPÜLLER (Y. I. S. I., 1899, ii., 482).—After dissolving in HNO_3 , the samples are boiled in a paraffin bath (135° C.) before comparing.
438. STEAD (Y. I. S. I., 1883, 213; and C. N., xlvii., 285).—Dissolve 1 grm. in HNO_3 , add excess NaHO , and compare filtrate with similarly treated standard steel. Moderate excess of heating, HNO_3 and NaHO are without influence. HCl must be avoided. Hardened steels give less colour.
439. HUNT (Y. I. S. I., 1883, 764).—The mechanical state of division of standard and sample should be alike. Stead's modification the more reliable under variable conditions. The colour is darker the more quickly the sample is dissolved. Instructions for very quick testing.
440. PARKER (C. N., xlii., 88).—C exists in different conditions, so that steels containing same percentage give varying degrees of colour. The test is modified to meet this difficulty.
441. HOGG (C. N., xlii., 131).—Paper on same lines as Parker's. In hardened steel there is a form of C and iron "which is decomposed by HNO_3 without communicating any colour whatever."
442. HOGG (Y. I. S. I., 1896, ii., 179).—Classification of C existing in steel. Speculation concerning the carbon of hardened steel which evades the colour test. By continued heating, Eggertz colour is

destroyed and CO_2 evolved. Saniter connects the missing C with the sub-carbide Fe_{24}C , Sauveur with the presence of martensite.

443. GALBRAITH (Y. I. S. I., 1881, 234).—Hammering, rolling, hardening, and annealing interfere with the colour test. Conditions must be strictly comparative.
444. WOODCOCK (Y. I. S. I., 1882, 111).—Both P and Si introduce negative errors. Carbonaceous gases are given off on dissolving hardened steel.
445. PARRY and MORGAN (C. N., lxvii., 176).—Not reliable for hardened or high per cent steels. Artificial standards no use.
446. ROBINSON (Y. I. S. I., 1887, ii., 363).—Artificial standards made from CoCl_2 , CuCl_2 , Fe_2Cl_6 , and HCl .
447. UKENA (Y. I. S. I., 1891, ii., 323).—Samples cooled in hot soapy water can be drilled as though cooled in air.

IV.b. Tintometers and other Apparatus.—

448. LEEDS (C. N., xxxvii., 229).
449. STEAD (Y. I. S. I., 1883, 217; and C. N., xlvii., 285).
450. RIDSDALE (Y. S. C. I., 1886, 585).—With some notes on Stead's modified colour process.
451. RIDSDALE (Y. S. C. I., 1888, 70).—A simplified apparatus for deep tints.
452. LOVIBOND (Y. S. C. I., 1888, 424).
453. McMILLAN (Y. I. S. I., 1894, ii., 157).—Refers to previous instruments and describes two new ones.
454. KRÜSS (Y. C. S., lxvi., ii., 158).
455. ZANGEMEISTER (Y. C. S., lxx., ii., 404).
456. REDWOOD (Y. S. C. I., 1885, 76).
457. ARNOLD (C. N., l., 25).—Bath of glass; perforated lid of glazed earthenware. Tubes can be suspended any depth in the solution.
458. KELSALL (C. N., l., 56).—A copper bath. Burnt sugar standards kept for years.

V. OTHER PROCESSES OF ESTIMATING CARBON.

459. DUPRE (C. N., xxxix., 39).—Pass CO_2 into solution of basic lead acetate. The cloud formed is compared with standard clouds. Very delicate.
460. CLERC (Y. I. S. I., 1885, 274).—Liberate C with CuSO_4 , oxidise with CrO_3 , and pass CO_2 through tubes containing KHO and a little manganate. An excess of CO_2 forms permanganate; the number of tubes thus changed indicates the amount of C.
461. VOLMER (Y. I. S. I., 1895, ii., 587).—Reiper's process consists in making a metallic streak on unglazed porcelain, treating it with cuprammonium chloride, and comparing with standards.
462. TROPENAS and WELLS (Y. S. C. I., 1892, 636).—The CO_2 in converter gases is proportional to the C in the metal. This CO_2 is determined, and the C deduces in less than a minute. The process is patented.

VI. ESTIMATION OF GRAPHITE.

463. SHIMER (C. N., lxxiii., 31).—By decomposing with HCl or H_2SO_4 high results are obtained due to titanium and other carbides in the residue. These carbides are easily soluble in HNO_3 .
464. TOSH (C. N., xvi., 168).—Separate Fe with HCl , and wash residue with alcohol and ether to remove hydrocarbons. In separating Si with NaHO there is always effervescence due to oxidation to silicic acid.
465. EGGERTZ (C. N., xviii., 232).—Decompose with H_2SO_4 and HNO_3 , evaporate, and re-dissolve in HCl . Dry filtered graphite and SiO_2 on tared filter at 100° C. Loss on ignition = graphite.
466. PIESSE (C. N., xxix., 57).—Very much like 465. Dries at 212° .
467. ALLAN (C. N., xxix., 91).—Criticism of Piesse's paper. Dissolve in HCl . Silicon and carbon com-

- pounds removed with KHO, and graphite determined by loss on ignition of the strongly dried residue.
468. MACKINTOSH (C. N., li., 147).—To estimate graphite in minerals, fuse with KHO, wash residue with HCl, &c., dry, and weigh.
469. HOCK (Z. I. S. I., 1882, 324).—Ignite residue under charcoal cover in a tared crucible; weigh, ignite, and determine graphite by loss. Ignite the separated filter-paper, and from the residue calculated the graphite which adhered to the paper according to the ratio $\frac{\text{graphite}}{\text{ash}}$ established by the burning of the bulk of the graphite.
470. CROBAUGH (Z. I. S. I., 1894, ii., 488).—Collect on counterpoised filters; remove SiO_2 with HF and HNO_3 ; digest with $(\text{NH}_4)\text{HO}$ to remove carbonaceous compounds.
471. TAMM (Z. I. S. I., 1887, ii., 361).—Dries separated graphite at 100° , and divides residue, after ignition, by 0.94 to allow for water in SiO_2 .
472. PARRY (C. N., lxvii., 247).—Separate Fe with HCl, wash residue with KHO, alcohol, and ether; mix with CuO and burn in O, or dry on weighed paper at $100\text{--}120^\circ\text{C}$.
473. STOLBA (Z. S. C. I., 1888, 235).—The combustion of graphite is promoted by mixing with silver dust.
474. WIDMER (Z. C. S., lviii., 923).—Cross and Bevan's observation that with CrO_3 part of the C is gasified as CO is true for graphite. To avoid error (5 per cent) the gases are passed over CuO.
475. SHIMER (C. N., lv., 231).—To sample graphitic irons moisten borings with alcohol, remove a portion, dry and weigh.* (See also Z. I. S. I., 1889, ii., 472).

VII. MISCELLANEOUS NOTES.

476. WARREN (C. N., xiv., 85).—An interesting account of the combustion of organic bodies in oxygen.
477. BERTHELOT (C. N., xix., 113).—"Immediate Analysis of Different Varieties of Carbon."
478. LEDEBUR (C. N., xlvii., 107).—To remove grease from the sample ignite in a current of dry nitrogen.
479. RAWSON (C. N., xlix., 161).—"The Estimation of Cuprous Chloride in Copper Liquors."
480. DONALD (C. N., lxiii., 73).—By rusting, pig-iron drillings lose a portion of their graphite.
481. LEEDS (Z. I. S. I., 1881, 658).—"Burnt" steel contains the same amount of C as the same steel before burning.
482. HEMPEL (C. N., lxix., 277).—Processes for estimating C classified and criticised. Ullgren (409), Weyl (334), and Wöhler's (378) processes preferred.
483. LEDEBUR (Z. I. S. I., 1894, i., 603).—Direct combustion of grey pig gives low results. Juptner's method (319) gives low results, due to escape of hydrocarbons. With Sarnström's modification (414) the results are accurate. Similar remarks apply to wet combustion of the C residue. Removal of Fe by cuprammonium chloride unsatisfactory. Separation of Fe with Cl most accurate if well done. HNO_3 preferable to HCl for separating Fe and graphite.
484. GÖTTIG (Z. I. S. I., 1894, i., 607).—Dry direct combustion inaccurate. Juptner's process (319) available if much CrO_3 is used. Cu and C need not be separated for wet combustion; must be for dry. Processes separating the iron and burning the residue in the dry way are inaccurate.
485. DOUGHERTY (Z. I. S. I., 1897, i., 573).—In FeSi compounds determines Fe, Si, Mn, S, and P, and then calculate the carbon by difference.
486. TABARY (Z. I. S. I., 1895, i., 492).—Irregular distribution of carbon in pig-iron.
487. LUZI (Z. I. S. I., 1893, ii., 334).—Graphite, so-called, may contain "graphitic" also. They behave differently with nitric acid.
488. LEDEBUR (Z. I. S. I., 1889, i., 368; and 1893, ii., 53).—Distinguishes hardening C, carbide C, graphitic temper C, and graphite; their properties and means of estimating them.
489. LEDEBUR (Z. I. S. I., 1891, i., 364).—Analysis of variously treated iron and steels, including graphite, graphitic temper carbon, hardening carbon, and carbide carbon.
490. JUPNER (Z. I. S. I., 1897, i., 248).—Estimates hardening and carbide C by a modification of the colour test. Summary of Osmond and Werth's investigation of the colour test. Graphite is oxidised on boiling with HNO_3 . Bamber (p. 266) vigorously criticises the methods. (See also p. 554).
491. DIXON (Z. C. S., lxix., 774).—"Mode of Formation of CO_2 in the Burning of Carbon Compounds."
492. ABEL and DEERING (C. N., xlvii., 200).—Carbon exists in cold rolled steel as Fe_3C . It is separated with a dilute solution of CrO_3 and H_2SO_4 . See also MULLER (Z. I. S. I., 1895, i., 495). ARNOLD and READ (Z. C. S., lxv., 788), and MYLIUS, FOERSTER, and SCHOENE (Z. C. S., lxii., ii., 39).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

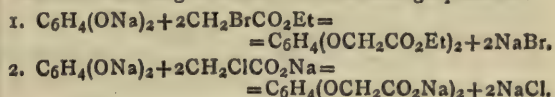
Ordinary Meeting, June 21st, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

(Concluded from p. 34).

98. "The Oxyphenoxy- and Phenyleneoxy-acetic Acids." By W. CARTER and W. TREVOR LAWRENCE.

The phenyleneoxyacetic acids, $\text{C}_6\text{H}_4(\text{OCH}_2\text{CO}_2\text{H})_2$, are obtained according to either of the following equations:—

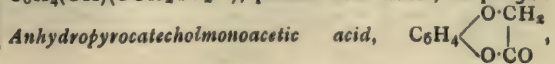


The condensation according to the first equation is not complete in the cases of resorcinol and hydroquinol, and a certain amount of acid ester, $\text{C}_6\text{H}_4(\text{OH})(\text{OCH}_2\text{CO}_2\text{Et})$, corresponding to the oxyphenoxyacetic acids, is formed, and may be separated from the neutral ester by potash solution.

On pouring the esters into alcoholic potash the potassium salts of the acids are precipitated as microcrystalline powders, which when acidified yield the free acids.

The amides are obtained from the esters by shaking with aqueous ammonia, the aniline salts result on boiling the acids with a benzene solution of aniline, and the anilides are obtained by heating the acids to 190° with aniline.

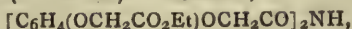
Pyrocatechol Derivatives.—Ethyl pyrocatecholdiacetate, $\text{C}_6\text{H}_4(\text{OCH}_2\text{CO}_2\text{Et})_2$, boils at $230\text{--}232^\circ$ (30 m.m.). Pyrocatecholdiacetic acid, $\text{C}_6\text{H}_4(\text{OCH}_2\text{CO}_2\text{H})_2$, needles from water, m. p. 178° . Aniline salt, m. p. 250° . Barium salt, $2(\text{C}_{10}\text{H}_9\text{O}_6\text{Ba})\cdot\text{H}_2\text{O}$. Pyrocatecholdiacetanilide, $\text{C}_6\text{H}_4(\text{OCH}_2\text{CONHPh})_2$, m. p. 196° . Pyrocatecholdiacetamide, $\text{C}_6\text{H}_4(\text{OCH}_2\text{CONH}_2)_2$, m. p. 203° . Ethyl pyrocatecholmonoacetate, $\text{C}_6\text{H}_4(\text{OH})(\text{OCH}_2\text{CO}_2\text{Et})$, b. p. 155° (30 m.m.). Pyrocatecholmonoacetic acid, $\text{C}_6\text{H}_4(\text{OH})(\text{OCH}_2\text{CO}_2\text{H})$, prisms from water, m. p. 152° .



* Converted bar should be sampled by boring clean through the bar and using all the borings. Steel faced articles, such as "draw plates," may be examined by taking a broad thin cut from each face and a small hole quite through. The data from the three samples enables one to calculate the depth of steel facing.

prisms from ligroin, m. p. 57°. *Pyrocatecholmonoacetanilide*, $C_6H_4(OH)(OCH_2CONHPh)$, m. p. 161°. (Compare Moureu, *Bull.*, 1899, [3], xxi., 107).

Resorcinol Derivatives.—*Ethyl resorcinodiacetate*, $C_6H_4(OCH_2CO_2Et)_2$, m. p. 42° (B. 40°), b. p. 228° (32 m.m.). *Resorcinodiacetic acid*, $C_6H_4(OCH_2CO_2H)_2$, m. p. 195°. The silver, copper, and iron salts are amorphous, the calcium and barium salts crystalline. *Aniline salt*, m. p. 137°. *Resorcinodiacetanilide*, $C_6H_4(OCH_2CONHPh)_2$, m. p. 169° (B. ca. 182°). *Imidoester*,—



m. p. 43°. *Resorcinodiacetamide*, $C_6H_4(OCH_2CONH_2)_2$, m. p. 167°. 2 : 4 : 6-*Trinitroresorcinodiacetic acid*, $C_6H(NO_2)_3(OCH_2CO_2H)_2$, is formed by boiling resorcinodiacetic acid with nitric acid, m. p. 174°, converted by potash at 140° into atyphnic acid. *Resorcinmonoacetic acid*, $3(C_8H_8O_4) \cdot H_2O$, m. p. 158°, anhydrous needles from toluene, m. p. 160° (B. 158°). *Resorcinmonoacetanilide*, m. p. 125°.

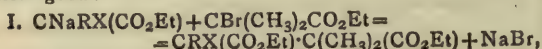
Hydroquinol Derivatives.—*Ethyl hydroquinoldiacetate*, $C_6H_4(OCH_2CO_2Et)_2$, needles from ligroin, m. p. 72°. *Hydroquinoldiacetic acid*, $C_6H_4(OCH_2CO_2H)_2$, prisms insoluble in all solvents tried except acetic acid, m. p. 251° (B. ca. 246°). *Hydroquinoldiacetanilide*, $C_6H_4(OCH_2CONHPh)_2$, m. p. 270°. The ammonium salt crystallises in needles from water. The silver and copper salts are amorphous, and the calcium and barium salts crystalline.

Hydroquinolmonoacetic acid, $3(C_8H_8O_4) \cdot H_2O$, prisms from water, anhydrous needles from toluene, m. p. 152°. *Aniline salt*, m. p. 119°. *Hydroquinolmonoacetanilide*, $C_6H_4(OH)(OCH_2CONHPh)$, m. p. 101°.

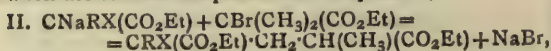
The melting-points in brackets, and indicated by B, refer to a private communication from Prof. C. A. Bischoff, who is engaged in the investigation of many of these substances, in pursuance of his "Studies on Condensations," and to whom we therefore relinquish their further study.

99. "The Condensation of Ethyl α -Bromoisobutyrate with Ethyl Malonates and Ethyl Cyanacetates: α -Methyl α' -Isobutylglutaric Acid." By W. TREVOR LAWRENCE, B.A., Ph.D.

The author showed that the following general reactions hold good:—



when the sodium compound is in suspension,

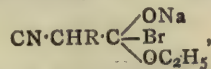


when the sodium compound is in solution,

where R=H or an alkyl group; X=(CN) or (CO_2Et) .

The behaviour of ethyl bromoisobutyrate is probably influenced by the degree of ionisation of the sodium compound.

The author suggests that the hydrobromic acid liberated from the bromoisobutyric ester combines with (the enolic form of) ethyl sodiomalonate or -cyanacetate to form a hypothetical addition compound; for example,—



which condenses with the unsaturated ester with separation of sodium bromide.

The following substances were isolated and investigated in the course of this research:—

I. In the condensation of ethyl sodioisobutylmalonate with ethyl α -bromoisobutyrate, or ethyl α -methacrylate in alcoholic solution.

Ethyl α -methyl- α' -isobutylpropanetricarboxylate, $CH(CH_3)CO_2Et \cdot CH_2 \cdot C(CH_3)(CO_2Et)_2$, b. p. 185° (18 m.m.), converted by hydrolysis with alcoholic potash into the potassium salt of a *methyl- α' -isobutylpropanetricar-*

oxylic acid. This acid melts at 167–168° (with evolution of carbon dioxide and formation of *cis*- and *trans*-methylisobutylglutaric acids).

The *cis*- and *trans*-methylisobutylglutaric acids, $CH(CH_3)(CO_2H) \cdot CH_2 \cdot CH(C_4H_9)CO_2H$, are best separated by crystallisation from boiling ligroin (b. p. 110–120°).

cis-Acid, m. p. 121°. *Anhydride*, a liquid, b. p. 196° (50 m.m.). *Anilic acid*, $C_{16}H_{23}O_3N$, m. p. 164°.

trans-Acid, m. p. 86–87°. *Anhydride*, a liquid, b. p. 178° (22 m.m.). *Anilic acid*, m. p. 196°.

The *trans*-acid may be converted into the *cis*-modification by heating with hydrochloric acid in a sealed tube, or into the *cis*-anhydride by distillation or by heating with acetic anhydride to 220°.

II. In the condensation of ethyl sodioisobutylcyanacetate, b. p. 165° (50 m.m.), with ethyl bromoisobutyrate or ethyl α -methacrylate in alcoholic solution: in the condensation of ethyl sodiocyanacetate with ethyl methacrylate and subsequent addition of isobutyl bromide.

Ethyl α -methyl- α' -isobutyl- α' -cyanoglutarate, $CH(CH_3)CO_2Et \cdot CH_2 \cdot C(CH_3)(CN)(CO_2Et)$, b. p. 196° (25 m.m.), on hydrolysis with alcoholic potash is converted into the potassium salt of a substance, $C_{11}H_{17}O_4N$, which melts at 164°, with evolution of carbon dioxide. This substance is possibly a mixture of methylisobutylcyanoglutaric acid with the monocarboxylic acid of methylisobutylglutarimide, as on distillation (295°, 760 m.m.) the imide (m. p. 78°) of the *cis*-acid (insoluble in sodium carbonate) and the nitrile of the *trans*-acid are obtained.

It is converted by hydrochloric acid into a mixture of *trans*-glutaric acid and *cis*-glutarimide.

The complete hydrolysis of the nitrile or imide is effected by 50 per cent sulphuric acid.

III. In the condensation of ethyl bromoisobutyrate with ethyl sodioisobutylmalonate or -cyanacetate in benzene solution: in the condensation of ethyl bromoisobutyrate with ethyl sodiocyanacetate in alcoholic solution with subsequent addition of isobutyl bromide,

Ethyl α -dimethyl- α' -isobutyl α' -cyansuccinate, b. p. 180° (20 m.m.), $CO_2Et \cdot C(CH_3)_2 \cdot CH(C_4H_9)(CN)(CO_2Et)$, when hydrolysed with alcoholic potash and then acidified, gives a pasty mass of cyano-acid—on complete hydrolysis with 50 per cent sulphuric acid it gives *α -dimethyl- α' -isobutylsuccinic acid*, $CO_2H \cdot C(CH_3)_2 \cdot CH(C_4H_9)CO_2H$, prisms from water, m. p. 141°.

Experiments on the oxidation of methylisobutylglutaric acid (the study of which was the original object of this research) with potassium permanganate either at 60° or in the cold, showed that the greater part of the acid could be recovered unchanged, the oxidation products consisting of oxalic acid, isobutylmalonic acid, a fatty acid (isobutylacetic acid?), two liquid acids, of which one appeared to be a hydroxy-acid, $C_{10}H_{18}O_5$, and the other an unsaturated acid, $C_{10}H_{16}O_4$, and a crystalline acid, m. p. 80°, of the same composition.

These acids were obtained in very small quantities and their complete separation was both difficult and probably unsuccessful.

100. "Methylisoamylsuccinic Acid." II. By W. TREVOR LAWRENCE, B.A., Ph.D.

The anil of *trans*- α -methyl- α' -isoamylsuccinic acid melts at 118°, and that of the *cis*-acid at 116°.

The partial conversion of the *cis*- into the *trans*-modification may be brought about by heating with hydrochloric acid, and the reverse change by heating the *trans*-acid with acetic anhydride at 210°.

The *cis*-anhydride is converted by phosphorus pentabromide, bromine, and alcohol into ethyl α -bromo-methylisoamylsuccinate (b. p. 155°, 20 m.m.), $C_{14}H_{25}O_4Br$, which, when poured into hot alcoholic potash, forms the potassium salt of isoamylcitraconic acid, $CO_2H \cdot C(CH_3) \cdot C(C_5H_{11}) \cdot CO_2H$.

Oxidation of methylisoamylsuccinic acid by means of

potassium permanganate gave results similar to those obtained by the oxidation of the isomeric methylisobutylglutaric acid (compare preceding abstract); only a small portion of the acid was oxidised by the permanganate, giving oxalic acid, a liquid acid having the formula $C_{10}H_{16}O_4$, and a lactic acid having the same formula and melting at 103° .

Correction.—Isoamylsuccinic acid melts at 83 – 84° , not 76° as previously stated (*Proc.*, 1899, xv., 163).

101. "The Estimation of Furfural." By WILLIAM CORMACK.

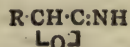
The process proposed by the author is based on the oxidation of furfural to pyromucic acid by means of an ammoniacal solution of silver oxide according to the equation $C_5H_4O_2 + Ag_2O = C_5H_2O_3 + 2Ag$. The action takes place quantitatively when the solutions are warmed. A known volume of a decinormal silver oxide solution, somewhat in excess of that required for the oxidation of the furfural, is added to the furfural solution, the reduced silver is filtered off through asbestos, and the silver remaining in the filtrate estimated by means of decinormal ammonium thiocyanate.

The method is applicable to furfural solutions such as those derived from fibres by distillation with hydrochloric acid, the furfural being distilled over with steam from the solution after neutralisation with alkaline carbonate, and subsequent slight acidification with oxalic acid.

102. "The Constitution of Hydrogen Cyanide." By JOHN WADE.

When potassium cyanide is heated with alkyl potassium sulphates at a lower temperature than in the preparation of nitriles, the isomeric isocyanide is often the principal product. The author also has found that practically all the isocyanides can be converted into nitriles by the action of heat. The formation of nitriles in the above interaction is thus accounted for, and one of the arguments in favour of the nitrilic constitution of hydrogen cyanide disappears.

Isocyanides form crystalline products with aldehydes, probably homologous with the aldehyde cyanhydrins, for which the formula—



is suggested, as the ordinary formula does not account for their anomalous behaviour with alkalis. Compounds have in this way been obtained from acetaldehyde and benzaldehyde in conjunction with methyl-, ethyl-, and phenyl-isocyanides.

Isocyanides also form crystalline products with alkyl iodides in presence of alcohol. This interaction accounts for the non appearance of isocyanides, and probably for the formation of nitriles, when potassium cyanide is heated with alkyl iodides in presence of alcohol. Compounds of this class have been obtained from methyl-, ethyl-, propyl-, isopropyl-, butyl-, isoamyl-, and phenyl-isocyanides in conjunction with methyl, ethyl, propyl, isopropyl, isobutyl, and isoamyl iodides.

n-Propyl isocyanide, and *n*-butyl isocyanide do not appear to have been prepared before. They are formed by interaction of the alkyl iodides with silver cyanide, and boil respectively at 97 – 99° and 118 – 120° (uncorr.).

103. "Inhibiting Effect of Etherification on Substitution in Phenols." By HENRY E. ARMSTRONG and EDWARD W. LEWIS.

The inhibiting effect on substitution produced by introducing methyl, ethyl, or benzyl in place of the hydroxylic hydrogen in phenolparasulphonic acid has already been referred to (Armstrong, *Proc.*, 1899, xv., 177). At the last meeting of the British Association, it was pointed out that "benzoyl appears to exercise a very remarkable inhibitive effect, as preliminary experiments show that benzoylated phenolparasulphonic acid remains unattacked by bromine under conditions which involve the conversion of the unbenzoylated acid into tribromophenol." This observation

has since been confirmed, and the experiments have been extended in order to determine the effect of radicles generally. Besides benzoyl, phenylsulphonyl, $Ph \cdot SO_2$, benzylsulphonyl, $Ph \cdot CH_2 \cdot SO_2$, and the radicle of Reychler's camphorsulphonic acid, $C_{10}H_{15}O \cdot SO_2$, afford complete protection against bromine. Picryl, $C_6H_2(NO_2)_3$, also appears to behave like benzoyl, but owing to the instability of picrylphenolparasulphonate in aqueous solution it is difficult to determine the exact nature of the change effected by bromine. Acetyl, on the other hand, exercises an effect similar to that produced by methyl and ethyl; and the complex radicle phenacyl, $Ph \cdot CO \cdot CH_2$, derived from acetophenone, acts much in the same way as acetyl. Difficulty has been experienced in determining the influence of the isomeric radicle phenacetyl, $Ph \cdot CH_2 \cdot CO$, owing to the instability of the ether produced by it; apparently, it also resembles acetyl.

In order to ascertain whether a determining influence is exercised by hydrogen in association with the carbon atom which becomes attached to the phenolic oxygen, tertiary butyl was introduced into phenolparasulphonate. The effect produced by this radicle seems to be altogether different from that of either methyl or ethyl, because on treating the sulphonate with one molecular proportion of bromine, only monobromosulphonate is obtained, the sulphonic radicle remaining intact, but it is displaced by a second molecular proportion of bromine; the methyl and ethyl derivatives are, to a large extent, directly converted into the parabromophenol ethers. In view of this observation, it will be necessary to examine other alkyl derivatives.

104. "Bromination of Oxyazo-compounds." By HENRY E. ARMSTRONG and PERCY C. C. ISHERWOOD.

The observations recently made by Hewitt and Aston and by Auwers unquestionably prove that the compound formed by the interaction of phenol and a diazobenzene salt, behaves, in the main, as benzeneazophenol, and there is no doubt that the isodynamic hydrazone comes prominently into evidence only in the presence of acids; it is clear, however, that the equilibrium is easily disturbed in either direction, and that in such a case the constitution can only be finally inferred from physical rather than chemical properties.

The authors must confess to having been too much influenced by the extraordinary difference in the behaviour of this compound towards excess of bromine as compared with that of its ethylated derivative, but apparently it is not necessary to infer from this that the two are structurally different, as the principle developed by one of them in discussing the laws which govern substitution in benzenoid compounds suffice to afford an explanation of the dissimilarity.

The conversion of benzeneazophenol into benzeneazodibromophenol and its re-solution by excess of bromine into diazobenzene and tribromophenol are comparable with the conversion of phenolparasulphonic acid, first into the dibromosulphonate, and then into tribromophenol and sulphuric acid.

Ethylation exercises an inhibiting influence such as is referred to in the previous abstract, benzeneazophenetol being converted by bromine in presence of sodium acetate only into benzeneazomonobromophenetol. This compound is also formed when a solution of the phenetol in glacial acetic acid is brominated, but at the same time a "hydrobromide perbromide" is formed which is readily deprived of its bromine by reducing agents. In a previous note (*Proc.*, 1899, xv., 243), the mistake was made of inferring from observations made with this latter compound that benzeneazo-orthobromophenetol is an easily reducible substance.

As the separation of the azo-group from Hewitt and Aston's benzeneazodibromophenol by bromine is effected even in presence of sodium acetate, it cannot be argued that the scission is consequent on the formation of the hydrazone, and the stability of benzeneazophenetol

must therefore be ascribed to the change produced by displacing the hydroxylic hydrogen. The extreme readiness with which the compound assumes the hydrazone form is manifest from the fact that if the sodium acetate be omitted, and two molecular proportions of bromine are used, the substance being merely dissolved in acetic acid, benzeneazodibromophenol is mainly resolved into bromodiazobenzene and tribromophenol. Benzoylated benzeneazophenol, like benzoylated phenolparasulphonic acid, is unaffected by bromine.

Clearly it will be desirable to study further oxy- as well as amido-azo compounds from the points of view indicated in the preceding abstract.

105. "*Meta-sulphonation of Aniline.*" By HENRY E. ARMSTRONG and W. BERRY.

It has been pointed out by one of the authors that, "in order to produce meta-derivatives from amines, it is necessary to paralyse, as far as possible, the ordinary ortho-para-orientating influence of the amino-group, and to give opportunity for the attack to take place in the nucleus" (*Proc.*, 1899, xv., 177; compare *B. A. Report*, 1899, 685, § 11).

In the case of aniline, sulphuric acid alone appears to be capable of exercising the necessary protective influence, because if the sulphate be dissolved in a large excess of chlorosulphonic acid, the mixture may be heated to 30–40° C. without any appreciable amount of hydrogen chloride being evolved. Under these conditions, the chlorosulphonic acid is not a sufficiently powerful sulphonating agent to produce even the sulphamate. Consequently, if aniline sulphate be added to a sufficiently strong fuming sulphuric acid, it is in part converted into the meta-sulphonic acid, the nucleus apparently being directly attacked. It is therefore possible to convert aniline into either para- or ortho- or meta-sulphonic acid at will.

106. "*Phenylacetylchloramine and Analogous Compounds.*" By HENRY E. ARMSTRONG.

The author calls attention to the discrepancies in the descriptions given of the properties of phenylacetylchloramine, and discusses the manner in which it under goes isomeric change.

107. "*Benzylanilinesulphonic Acids.*" By IDA SMEDLEY. These acids have been prepared in order to compare their behaviour with that of the corresponding methyl and ethyl derivatives studied by Miss Evans (*Proc.*, 1895, xi., 235; 1896, xii., 234).

Anilineparasulphonic acid is readily benzylated by digesting an aqueous solution of its sodium salt with benzyl chloride and alkali, the mono- or di-benzyl derivative being formed according to the proportions used. The meta-acid is dibenzylated with extreme readiness.

In their behaviour with bromine, the dibenzylated closely resemble the dimethylated acids. It may therefore be assumed that benzyl does not promote the displacement of the sulphonic group as it does when introduced into phenolparasulphonic acid in place of the hydroxylic hydrogen, but it undoubtedly has an influence different from that exercised by either methyl or ethyl. Thus it is characteristic of dimethyl and diethylsulphanilic acids that, when acted on by bromine, each is converted into an ortho-brominated acid capable of combining with bromine to form a comparatively stable perbromide. The dibenzyl acid yields a similar mono-brominated acid, but this does not form a perbromide; it is, however, very easily deprived of its benzyl by the further action of bromine.

108. "*Benzeneorthodisulphonic Acid.*" By HENRY E. ARMSTRONG and S. S. NAPPER.

The authors have prepared benzeneorthodisulphonic acid by applying Leuckart's xanthate method (*J. pr. Chem.*, 1890, xli., 179, to parabromanilineorthosulphonic acid. A series of compounds has thus been obtained corresponding with those prepared by Miss Walter (*Proc.*, 1895, xi., 141) from sulphanilic acid.

Potassium parabromophenylxanthateorthosulphonate is easily soluble in water, from which it crystallises with 10 molecules of water.

When hydrolysed by means of sulphuric acid or alcoholic potash, it yields the corresponding thiophenolsulphonic acid, $C_6H_3Br(SH) \cdot SO_3H$, or its potassium salt, the thiophenotolsulphonate, $C_6H_3Br(SeH) \cdot SO_3K$ being also formed when it is hydrolysed by aqueous potash, and when it is decomposed by heating at about 200°.

Bromobenzene-3 : 4-disulphonic acid is conveniently prepared by directly oxidising the xanthate with potassium permanganate. Its sulphochloride crystallises in monosymmetric prisms melting at 88°. The amide crystallises in brilliant anorthic prisms; the anilide in monosymmetric plates melting at 182°. It is converted into benzeneorthodisulphonic acid by boiling its aqueous solution with soda and zinc dust.

Sodium benzeneorthodisulphonate is very soluble in water, from which it crystallises in long transparent prisms. The barium salt is sparingly soluble even in hot water, and crystallises in glistening plates.

Unlike 1 : 2-naphthalene-1 : 2-orthodisulphonic acid, but like toluene 3 : 4-disulphonic acid, benzeneorthodisulphonic acid is converted into the corresponding chloride by phosphorus pentachloride. This crystallises in magnificent monosymmetric prisms melting at 143°.

The corresponding amide and anilide also crystallise in monosymmetric prisms, the former melting at 252°, the latter at 241°.

A comparison of the acid with phthalic acid is being made.

109. "*An Isomeride of Furfurine.*" By J. P. MILLINGTON, B.Sc., and H. HIBBERT, B.Sc.

By the application of the method of Japp and Moir (*Trans.*, 1900, lxxvii., 637) for the preparation of isoamarine from amarine, the authors have succeeded in preparing an isomeride of furfurine. It crystallises from water in needles melting sharply at 143° (furfurine melts at 116°), and on analysis was found to correspond with the formula $C_{15}H_{12}N_2O_3$. A platinichloride and silver derivative have been obtained of which the formulæ are $(C_{15}H_{12}N_2O_3)_2H_2PtCl_6$ and $C_{15}H_{12}N_2O_3Ag$ respectively.

110. "*The Mono- and Di-acetyl and Phenacetyl Diethyl Tartrates.*" By J. McCRAE and T. S. PATTERSON.

The preparation of monoacetyl, diacetyl, monophenacetyl, and diphenacetyl diethyl tartrates was described. Considerable difficulty was experienced in the purification, and different methods had to be adopted in each case. The specific rotation of these substances has been determined at various temperatures with the following results:

Monoacetyl diethyl tartrate ..	$[\alpha]_D^{20} = +9.30^\circ$
Diacetyl " " ..	$[\alpha]_D^{100} = +6.30^\circ$
Monophenacetyl " " ..	$[\alpha]_D^{20} = +30.38^\circ$
Diphenacetyl " " ..	$[\alpha]_D^{20} = +17.92^\circ$

A comparison is instituted, on the one hand, between the series of monoacidyl tartrates, where it is shown that the phenacetyl radicle exerts a much greater influence than that exerted by the acetyl radicle, and, on the other hand, between the members of the series of diacidyl tartrates where the acetyl and phenacetyl radicles behave similarly but very differently from the toluyl radicles.

The regularity of the influence exerted by the successive introduction of two acidyl groups is noticed. The first acidyl group increases the rotation of the diethyl tartrate, but the second acidyl group diminishes the rotation of the monoacidyl compound.

Development and Propagation of the Explosive Wave.—H. Le Chatelier.—The author's experiments were performed on mixtures of acetylene with oxygen and the oxygen compounds of nitrogen, and on an explosive mixture of carbonic oxide and oxygen.—*Comptes Rendus*, cxxx., No. 26.

CORRESPONDENCE.

DISTILLATION WITHOUT BUMPING.

To the Editor of the Chemical News.

SIR,—In view of the number of twice-told tales that are continually finding their way into the literature of chemistry and other sciences it is doubtless time to make a glaring example of somebody, but in view of the numerous *able-bodied* Hawthornes in chemistry it does seem almost cruel, not to say cowardly, to select for this purpose the writer of the poor pitiful little pipe-stem squib that appeared in this journal under the above title, and we venture to predict that if the ghost who stuck the match to this victim would but dare to publish his name so that his writings could be reviewed from the same standpoint, he would thereafter do his haunting on some other planet.—I am, &c.,

DIAZO.

NOTICES OF BOOKS.

The Bacterial Treatment of Sewage; a Handbook for Councillors, Engineers, and Surveyors. By GEORGE THUDICHUM, F.C.S., &c. London: The Councillor and Guardian Offices. Pp. 92.

HITHERTO chemical treatment of some sort has occupied a prominent place in all books dealing with the subject of the purification of sewage. These methods of precipitation, sludge treatment, &c., are, according to our author, no longer considered, though the knowledge acquired during the past few years may cause the profitable utilisation of waste matters to be to some extent attainable.

Experience has shown that the best methods of sewage treatment depend on bacterial action in specially prepared areas. And, in the author's opinion, there are only two adaptations of this principle which have been proved of practical value. These two methods are the Sutton system and the septic tank, by either of which a constantly good result can be obtained in the simplest and cheapest possible manner.

The Sutton or aerobic system of sewage purification is the outcome of the experiments carried out by the Metropolitan Board of Works and the London County Council, between the years 1884 and 1896. In this method the sewage first passes through a grid, and then into a coarse-grained bacteria bed consisting of a tank filled with lumps of coke, broken bricks, clinker, &c., which will pass through a three inch ring, but no fine stuff; it is under-drained with open jointed drain-pipes leading to the discharge point. After filling with sewage the bed is allowed to stand for two hours; it is then emptied on to another finer-grained bed, and left for a similar time. In these beds the organic matter in solution is oxidised, and the suspended matter deposited; after discharging, the sludge remains in the bed, the interstices of which now being filled with air, the aerobic organisms are provided with all the conditions for rapid reproduction, the organic matters are rapidly attacked, and after a few hours the bed is ready for another charge. Practical experience has shown that these beds may work twice daily with advantage. The septic tank process devised by Mr. Donald Cameron differs principally from the Sutton system in that in the former case anaerobes, and in the latter case aerobes, are chiefly relied on to effect the solution of the suspended matter, and the preliminary breaking down of complex organic substances. The tank is made of such a size that the sewage takes from eighteen to twenty-four hours to pass through, and during this time the organic matter in suspension is dis-

solved by bacterial action in such a manner that the effluent leaving the tank is oxidised to the extent of some 50 per cent, while the whole is in a condition to be readily purified in the oxidising aerobic beds; these beds, by an ingenious device, have the filling, standing full, emptying, and resting empty for aeration regulated automatically.

Amongst other methods described by the author we may mention those of Scott, Moncrieff, Lowcock, Adeney, Waring, &c.; they all, however, are said to be inferior to the Sutton and septic tank systems, without producing better results.

The author also deals with the treatment of storm water, trade refuse liquors, and the land treatment of sewage, but the great merit of his book lies in the fact that it is the first book which deals solely with the modern bacteriological methods of sewage purification.

Elementary Inorganic Chemistry. Metals. By S. R. TROTMAN, M.A., F.I.C., &c. London: Rivingtons. 1900. Pp. 182.

THIS volume is intended as a continuation of the author's book on the non-metallic elements, and in a like manner it gives a selection of the more important facts concerning the elements dealt with, in a style suitable for a first course.

The metals and their principal reactions are first described separately; then in Chapters XI. to XV. the group arrangements are given with tables for making simple analyses.

The book is well arranged and clearly printed, and will make a useful laboratory companion for beginners.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxx., No. 26, June 25, 1900.

The Acidity of Alcohols.—M. de Forcrand.—The author recently determined the following influence coefficients for carbon and hydrogen:—

$$C = +3.01 \quad H = -2.85:$$

and from these obtained values for—



By means of these and other known numbers the following coefficients were obtained:—

Monatomic alcohols	..	+29.71 to 27.89	(from C to C ₅).
Glycol		+31.32	"
Glycerine		+32.28	"
Erythrite		+32.76	"

Hydrogenation of Ethylene in presence of various Reducing Metals.—Paul Sabatier and J. B. Senderens.—The series of experiments performed by the authors show that, in the same manner as reduced nickel, so reduced cobalt, copper, and iron are capable of inducing the hydrogenation of acetylene, but their activity is less. Whilst nickel reacts in the cold and indefinitely, cobalt only acts in the cold for a very limited time: when hot its action is tolerably rapid, but diminishes in proportion to the carburization of the metal. Copper acts still less quickly and only above 180°, but the action does not diminish, and can, under these conditions, effect the total hydrogenation after a considerable lapse of time. Iron is the slowest of all; above 180° even it acts slowly, and

its activity, very slight in the beginning, diminishes little by little.

Crystalline Compounds of Acetylene with Cuprous Chloride and Potassium Chloride.—M. Chavastelon.—In a previous paper the author showed how, by regulating the current of acetylene through a solution of cuprous chloride and potassium chloride, either yellow or colourless crystals can be obtained. He showed that it was easy to transform colourless into yellow crystals. The present paper contains the results of analysis of the two varieties of crystals after further purification. The colourless crystals correspond to the formula $C_2H_2(Cu_2Cl_2)_2KCl$, whilst the yellow ones are represented by $C_2H_2[(Cu_2Cl_2)_2KCl]_2$.

Oxidation of Anethol and Analogous Bodies (Isosafrol, Isoapiol, &c.).—J. Bougault.—By acting with iodine and yellow mercuric oxide in alcoholic solution on anethol, the latter is oxidised and transformed into an aldehyde, $C_{10}H_{12}O_2$, by fixation of an atom of oxygen. The same operation, made with bodies analogous to anethol, and like it containing a propenyl lateral chain, gives the same results. The author concludes therefore that the oxidation is effected on the propenyl lateral chain. The reaction can be represented by the equation, $C_{10}H_{12}O + HgO + I_2 = HgI_2 + C_{10}H_{12}O_2$. The reaction is quantitative and may serve as the base of a method of estimation of these bodies.

A New Derivative of Benzophenone.—MM. Chénier de Coninck and Derrien.—The authors investigate the action of several acids, violet and indigo light and ordinary sunlight on benzophenone. By dissolving benzophenone in pure methylic alcohol and exposing it to the sun's rays, beautiful crystals are obtained, melting at about 180° , and having no colour.

Composition of Compounds of Fuchsine with Colouring Matters, Acid by Constitution.—A. Seyewetz.—The author has already shown that compounds formed by the union of acid colouring matters with basic colours, are not only due to the particular nature of the acid groups or the substituted bases in these compounds. He now undertakes a more complete study of these compounds, limiting himself for the moment to those obtained with the well crystalline basic colouring matter fuchsine and acid colouring matters.

MISCELLANEOUS.

A Reaction of Acrolein and some other Aldehydes.—L. Lewin.—For the detection of acrolein the author has found that the following reaction may be made use of:—When piperidine is mixed with a solution of nitroprussiate of soda and acrolein, added either in solution or not, a gentian-blue colouration is produced; this colouration is intense, if the solution is at 0.1 to 1.0 per cent it is a pure blue, at 1/2000 it is perceptible, at 1/30000 the limit is reached, and the solution takes only a greenish colour. The blue colouration becomes violet on the addition of NH_3 , rose-violet on the addition of $NaOH$, greenish-blue with $C_2H_3O.OH$, rusty brown with a mineral acid, and dirty brown on the addition of H_2O_2 . In this reaction the piperidine can be replaced by dimethylamine, but the action becomes less sensitive. Other aldehydes, such as acetaldehyde, paraldehyde, propionaldehyde, and cinnamic aldehyde, give analogous colourations; with acetaldehyde in particular the reaction is very delicate, the limit of sensitiveness exceeding 1 in 12,000. Formic aldehyde, trichloraldehyde, isobutyric aldehyde, benzaldehyde, salicylic aldehyde, phenylacetic aldehyde, cenanthol, and furfural do not give any colouration with the above reagent.—*Berichte*, vol. xxxii., p. 3388.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Tungsten-Bronze.—Will some reader kindly inform me where tungsten-bronze may be bought?—HARRY BREARLEY, Totley, near Sheffield.

Starch Size.—I should be glad if any of your readers could inform me if there is any known purpose to which discoloured flour and starch size can be applied. I have a quantity regularly wasted.—T. B.

Aquarina Dye.—We should be much obliged if any reader can let us know the house of the aquarina dye, a new American product. This dye is of all colours, and is used by painters, and serves to dye metals, walls, &c.—LUIGI DE VIVO, Via Stella 107, Naples.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2123.

ON ELECTRIC TOUCH AND THE MOLECULAR CHANGES PRODUCED IN MATTER BY ELECTRIC WAVES.*

By JAGADIS CHUNDER BOSE, M.A., D.Sc.,
Professor of Physical Science, Presidency College, Calcutta.

(Continued from p. 42).

Mass Action and Molecular Action.

Of the attempts made to explain the action of contact-sensitiveness, Professor's Lodge's theory of coherence has been the most suggestive. The coalescence of water and mercury drops in Lord Rayleigh's experiments, and Professor Lodge's observation of the welding of two metallic spheres by powerful oscillatory discharge in the neighbourhood, apparently lend much support to the theory of electric welding, which explains in a simple manner the diminution of contact-resistance of various metallic filings when subjected to strong electric variation.

On this theory it follows that *all* imperfect contacts should exhibit a diminution of resistance when subjected to electric radiation. In carrying out a systematic investigation of the contact-sensitiveness of metals, I, however, found that there are substances, of which potassium may be taken as a type, which exhibit an increase of resistance. Potassium is not a solitary instance; I have found a large number of elements exhibiting this action; the number of compounds which exhibits a similar action is also considerable. Other experiments will be presently described which would show that the theory of coherence is inadequate. From the above it would appear that the subject is far more complex than was at first supposed. For various reasons it would be best to distinguish between the two different actions, which may conveniently be described as mass action and molecular action.

Mass Action.—By this is meant the general action, say, between two masses when placed in a very strong electric field. Under the given circumstance, sparking may take place between the bodies, and the two may thus be welded together. From what has been said it will be seen that such action is *non-discriminative*—that is to say, the action will be the same whatever the chemical or physical nature of the substance may be. The best way of showing this action is with drops of liquid, with surface contamination, for any incipient welding will be at once exhibited by the complete coalescence of the drops. The non-discriminative nature of the action is shown in a striking manner in the following experiment. I may mention here that fragments of solid potassium, and in a lesser degree sodium, exhibit an increase of contact-resistance under the action of electric waves. I made a liquid alloy of potassium and sodium, and drops of this alloy were allowed to float on the stratum separating dense Rangoon oil from lighter kerosine, the alloy being of an intermediate density. The drops coalesced when placed in an intense alternating electric field. The next experiment was made with potassium heated under melted (hard) paraffin. By stirring the molten K with a glass rod, the metal was broken up into numerous spherical drops. These also coalesced under similar electric influence. It is, however, to be borne in mind (1) that in the above experiment the substance is in the form of a liquid, and that in this particular condition certain important molecular changes, to be presently described,

cannot very well take place: (2) that the conditions of the experiment are abnormal.

Experiments will be presently described which will show that the observed variation of conductivity produced by radiation is not due to coherence, but to certain molecular changes of an allotropic nature.

Molecular Action.—By this I mean the allotropic modification produced in a substance by the action of electric waves, the allotropic change being due to a difference in the atomic or molecular aggregation. It will be shown that such molecular change does take place by the action of electric waves, and that all the observed effects of variation of resistance of the sensitive substance may be explained on the theory of allotropic transformation due to the above cause. The effect due to molecular changes in a substance is also expected to be modified by the chemical nature of the substance; thus the molecular action due to radiation, giving rise ultimately to the variation of conductivity of the sensitive substance, will be *discriminative*, in contradistinction to the non-discriminative mass action.

Is the effect of radiation due to non-discriminative coherer action or to the discriminative molecular action? That the effect is discriminative, and therefore molecular, appears to be decisively proved by the experiments described below. If further proofs are necessary, they are afforded by the characteristic curves of variation of current with the E.M.F. given by the three types of substances, positive, negative, and neutral; by the continuity of radiation effect on matter; and, lastly, by certain remarkable results I obtained, which show that the effect of ether waves on elementary substances depends on the chemical nature of the substance; in other words, the effect is found to be a periodic function of the atomic weight of the substance. A detailed account of the above will be given in a future paper.

On the Change of Sign of Response in the Receiver, due to a Variation of Intensity of Radiation.

After finding the increase of resistance exhibited by certain substances, I wished to see whether these showed any further difference as compared to substances which exhibit a diminution of resistance. In my determination of the "Index of Refraction of Sulphur for the Electric Ray" (*Proc. Roy. Soc.*, 1895), I used the method of total reflection. I often noticed that just before total reflection, when the intensity of the transmitted beam became comparatively feeble, the receiver indicated an increase instead of the usual diminution of resistance. Professor Lodge mentions in one of his papers that an iron filing coherer exhibits an increase of resistance when acted on by feeble radiation. Thus, if positive substances like iron give a negative reaction, with the diminution of radiation intensity, negative substances may be expected to give a positive reaction with feeble radiation. Very sensitive substances are, however, not so well adapted for an exhibition of this reversed action, possibly because the range of sensibility is comparatively great. But it is not difficult to demonstrate this property in the case of moderately sensitive substances.

The following experiment with a moderately negative substance (arsenic), and a moderately positive substance (osmium), will bring out this interesting peculiarity in a clear manner. The intensity of incident radiation may be varied in two ways—(1) by removing the radiator further and further from the receiver, or (2) by using polarised radiation, whose intensity may be varied by the rotation of an analyser. In the experiment to be described, the first method was adopted.

Experiments with Arsenic Receiver.—A receiver was made of freshly-powdered arsenic. The radiator used emitted radiation of strong intensity. It was at first placed close to the receiver, and there was produced a moderate increase of resistance. It was then removed further and further, and the increase of resistance became less and less. When the distance was increased to 25 cm. the action was reduced to zero. When the distance was

* A Paper read before the Royal Society, February 8, 1900.

increased to 30 c.m. there was a diminution of resistance, showing that 25 c.m. is, in this case, the *critical distance*. The receiver continued to exhibit a diminution until the radiator was removed to a distance of 70 c.m., when the radiation intensity was too feeble to affect the receiver. Now this critical distance may approximately be regarded as a measure of the sensibility of the substance. In this particular case the electric touch has a negative sign. If by any means (some of which will be described later on) the substance becomes more sensitive, *i.e.*, more negative, the critical distance will be increased. On the contrary, if the sensitiveness becomes less (the substance tending towards positive direction) the critical distance will be decreased. The application of this principle is of importance as affording a means of determining the variation of sensitiveness under different conditions.

Experiments with Osmium Receiver.—Substances which are feebly positive give a diminution of resistance when the radiator is close to the receiver, and an increase of resistance when the radiator is beyond the critical distance. Thus the critical distance for an osmium receiver (whose normal action is moderately positive) was found to be about 250 c.m. The radiator at a distance of 300 c.m. produced a deflection of -3 divisions in a galvanometer placed in the receiver circuit. But at the distance of 200 c.m. the deflection became $+4$, and at the reduced distance of 50 c.m. the deflection became $+150$ divisions.

In order to avoid confusion, we may choose to call the effect due to strong intensity of radiation as the normal action. The sign of normal action might further be verified, wherever possible, by obtaining a reverse action with feeble radiation intensity.

Molecular Changes produced in Matter by the Action of Electric Waves.

A sensitive receiver made, say, of iron powder, has its conductivity suddenly increased by the action of electric radiation; but the sensitiveness of the receiver is lost after the first response, and it is necessary to tap it to restore the sensitiveness. On the theory of coherence, the loss of sensitiveness is explained by supposing that electric radiation brings the particles nearer, and welds them together, and that the sensitiveness can then only be restored by the mechanical separation of the particles. This supposition, however, fails in the case of substances which exhibit an increase of resistance by the action of radiation. It may, however, be supposed that by some process, little understood, the particles are slightly separated by the action of electric waves, thus producing the observed increase of resistance. On this view, however, the restoration of sensitiveness by tapping remains unexplained. Again, if the increase of resistance is due to a slight separation of particles, suitable small increase of pressure ought to restore the original conductivity, as also the sensitiveness. It is, however, found that a considerable pressure is required to restore the original current, as if the outer layers of the particles were rendered partially non-conducting by radiation, and had to be broken through before the original current could be re-established. It is also found that though the sensitiveness is restored by this expedient of increasing the pressure, yet the restoration is only partial, and that after a repetition of this process the receiver loses its sensitiveness almost completely.

I have attempted to find out an explanation of this obscure "fatigue" effect. This subject will best be treated in connection with the anomalous behaviour of silver, which I find is also in a manner connected with the fatigue effect. Silver, when subjected to radiation, exhibits, as indicated in my last paper, sometimes an increase, and at other times a decrease, of resistance. The difficulty in this case cannot be explained on the supposition of variations of radiation intensity, as the anomaly persists even when the intensity of radiation is maintained uniform by keeping the radiator at a fixed distance.

In order to explain these actions, I assumed the following hypotheses, which, with the necessary deductions, are given below:—

- (1). That electric radiation produces molecular change or allotropic modification in a substance.
- (2). That, starting from the original molecular condition A, the effect of radiation is to convert it, to a more or less extent, into the allotropic modification B (the latter condition will be designated as the "radiation product"). It follows that this change from one state to the other must be accompanied by a corresponding change in the physical properties of the substance.
- (3). As one of the properties of a substance is its electric conductivity, any allotropic changes produced by radiation should be capable of being detected by a variation in the conductivity of the substance.
- (4). As a molecular strain is produced during transformation from A to B, at a certain stage there may be a rebound towards the original state A. Thus, after the molecular change from A to B condition has reached a maximum value, the further action of radiation may be to re-convert, to a more or less extent, B to A, this reversal of effect being indicated (see No. 3) by a corresponding electric reversal.

(5). That the ultimate loss of sensitiveness, known as "fatigue," is due to the presence of the radiation product, or strained B variety, along with the A variety, the opposite effects produced by the two varieties neutralising each other.

The justification for the above hypotheses is to be sought for:—

- (1). From analogy with other known radiation phenomena.
- (2). From experimental proof—
 - (a). Of the allotropic transformation being attended with changes in the conductivity of the substance.
 - (b). Of the existence (and, if possible, the production by chemical means) of an allotropic modification analogous to the radiation product or B variety, whose reaction should be opposite to that of the substance in a normal condition (A variety).
 - (c). Of the assumption that after the maximum transformation of A into B, the further action of radiation is to re-convert, to a more or less extent, the form B into A, such transformations giving rise to electric reversals.
 - (d). Of the existence of the radiation product in a fatigued specimen.

The above mentioned hypotheses will obtain still stronger support if further deductions from the above theory are borne out by confirmatory experiments.

I will now describe investigations on the lines sketched above.

Allotropic Modification produced by Visible Radiation.

As regards the action of radiation in producing allotropic modification, several such instances are known in the case of visible radiation. In the familiar example of the conversion of yellow phosphorus into the red amorphous variety, the effect is quite apparent. But this is not the case in the transformation of the soluble sulphur into an insoluble variety by the action of light; here the transformation is not apparent, and has to be indirectly inferred from the insolubility of the solarised product in carbon bisulphide. The reason why a far larger number of instances of allotropic transformation produced by light is not known is not because that such effects are not more numerous, but because we are unable to detect such changes. It must be admitted that our knowledge of molecular changes, specially in a solid, and the means of their detection, is at present extremely limited.

Variation of Conductivity produced by Allotropic Changes.

There is one method of detecting these molecular variations to which little attention has hitherto been

given, but which appears to be of great interest, and promises to yield important results in investigations of this class. It is evident that changes in molecular structure must be attended with changes of physical properties, electric conductivity being one of them. Among other instances of allotropic changes attended with changes in electric conductivity may be mentioned the wide difference of conducting power between graphite and diamond. The same great differences of conductivity is seen between the crystalline and amorphous varieties of silicon, and between the "metallic" and white varieties of phosphorus. But it is not at all necessary to take only such extreme cases to show the influence of molecular or atomic aggregation in influencing the conductivity. This effect is brought into painful prominence by the variation produced in spite of all precautions in our standards of resistance.

Experimental Proof of Allotropic Changes being attended with Variation of Conductivity.—I shall now describe a direct experiment by which the change of conductivity produced in a substance by molecular change is exhibited. Red mercuric iodide is converted into the yellow variety by the application of heat, and the substance does not return to its original state till after a considerable lapse of time. The recovery here is very slow. A small quantity of mercuric iodide was now placed in a tube provided with sliding electrodes, and a current was made to pass through the substance by suitable compression. The conductivity of the substance is rather small, and therefore a thin stratum should be taken for experiment. The current is observed by means of a delicate galvanometer. On the application of heat to the tube (which converts the red into the yellow variety), there was at once produced, simultaneously with the molecular transformation, an increase of conductivity. This effect is not due to a rise of temperature, for the increased conductivity was still exhibited on cooling the tube. From this experiment it is seen that the molecular changes can be inferred from changes in the conductivity. In the case described above, the recovery from the B, or second stage, to the first stage, A, is slow; but there may be substances (and there are such substances) where, under the given conditions of temperature and other physical surroundings, the first stage is far more stable than the second; the substance will then pass back quickly from the B condition to the primitive state, on the cessation of the exciting cause, which gave rise to the transient B effect. The substance will in this case be "self-recovering."

(To be continued).

THE ESTIMATION OF LEAD BY ELECTROLYSIS OF THE SULPHATE AND THE CHLORIDES. APPLICATION TO THE ANALYSIS OF LEAD GLASSES AND CHROMATES OF LEAD.

By CH. MARIE.

THE two principal methods for the separation of lead, founded on its precipitation by sulphuretted hydrogen or sulphuric acid in the presence of alcohol, bring it to the form of sulphide or sulphate, which is not adapted to electrolytic estimation on account of its insolubility in dilute nitric acid. As nitric acid easily transforms the sulphide into the sulphate I only considered the case of this latter salt.

To effect the solution of sulphate of lead in nitric acid, I decided, after several experimental trials, to use nitrate of ammonia, a reagent which does not introduce any fixed substance, and which can be easily eliminated in the subsequent analytical operations. This solution was made in the following manner:—

The sulphate of lead is placed in the beaker in which it

is to be electrolysed, and attacked with nitric acid to which crystals of nitrate of ammonia are gradually added. To hasten the solution it is heated on a water-bath. When all the sulphate is dissolved the solution is diluted with warm water, and the electrolysis is proceeded with in the ordinary manner, keeping the temperature up to 60–70°. The quantities of the reagents necessary are as follows:—For 0.3 grm. of sulphate it is necessary to have 5 grms. of nitrate of ammonia; as for the nitric acid, its quantity is determined by this condition, viz., that after dilution the liquid ought to contain 10 per cent of free acid.

As the sulphate dissolves more easily in acid which has been slightly diluted than in concentrated acid, it is as well before adding the latter, to pour a little water over the sulphate. In three hours, with an unpolished platinum electrode having a surface of 90 square c.m., and with a current of 0.3 ampère intensity, we can easily deposit 0.4 grm. of binoxide of lead.

This method allows of the application of electrolysis to the analysis of lead glass. It is sufficient to attack the finely powdered glass with hydrofluoric acid containing the necessary quantity of sulphuric acid to transform the bases into sulphates. Too great an excess of sulphuric acid will prevent the solution of the sulphate of lead, which should be carried out as described above. After the electrolysis we can proceed immediately to the estimation of the alkaline metals, if the material under examination contains no metal of the iron group, or of the alkaline-earth group.

Estimation of Lead in the Chromates.—The chromates of lead dissolve still more easily than the sulphates in the mixture of nitric acid and nitrate of ammonia. For 0.5 grm. of chromate 2 grms. of nitrate suffice; as for the nitric acid, it is sufficient for the final solution to contain 10 per cent.

The electrolysis is conducted as in the case of the sulphate; the chromic acid, during the operation, is completely brought into the state of sesquioxide of chromium, directly precipitable by ammonia.

By the simplicity of the analytical method and the exactness of the results furnished, this method will be very useful for the analysis of such important commercial products as the silicates and chromates of lead.—*Bull. Soc. Chim.*, Series 3, vol. xxxii., No 12.

On Nitracetone.—Ad. Lucas.—Following up a previous publication the author now announces that he has obtained nitracetone in a crystalline form. For this purpose he dilutes the solution of nitrite of silver and iodacetone in ether with a quantity of ether so as to obtain a not too thick liquid; this is kept agitated at 0° until the odour of iodacetone has disappeared, which requires about twenty-four hours. The solution is then filtered and washed with a little ether, then washed a second time with ether in another flask until no residue is left on evaporating the washings to dryness; it is in this second portion that the pure nitracetone is found, while the ether used for the first washing contains the secondary products. On evaporating the second portion of ether, well-formed crystals are obtained, easily soluble in benzene, from which the pure nitracetone separates in the form of beautiful needles. It crystallises in benzene in large plates, is fairly soluble in water, and more easily so in alcohol and ether; it fuses at 49°. The aqueous solution of nitracetone is distinctly acid. The author describes its ammonium salt, $\text{CH}_3\text{CO.CH:NO.ONH}_3$, as well as the phenylhydrazone, $\text{CH}_3\text{C(N}_2\text{H}_5\text{C}_6\text{H}_5\text{)CH}_2\text{NO}_2$. The proof that the substance $\text{C}_3\text{H}_5\text{NO}_3$ obtained by the author is the true nitracetone, $\text{CH}_3\text{CO.CH}_2\text{NO}_2$, or rather the isonitracetone, $\text{CH}_3\text{CO.CH=NO.OH}$, and not its isomer the nitrite of ethylcarbinol, $\text{CH}_3\text{CO.CH}_2\text{O.NO}$, is furnished by the fact that it gives, on reduction, amidoacetone $\text{CH}_3\text{CO.CH}_2\text{NH}_2$.—*Berichte*, vol. xxxii., p. 3179.

THE
EIGHTH GROUP OF THE PERIODIC SYSTEM
AND SOME OF ITS PROBLEMS.*

By JAS. LEWIS HOWE.

(Concluded from p. 39):

Of the simple salts of oxy-acids few are known of any metals of this group except the lower series, iron, cobalt, and nickel; a single sulphate of rhodium, one of palladium, and perhaps a double sulphate of platinum, a chromate of iridium, a basic carbonate of palladium, two or three nitrates, a phosphate of rhodium, and a hypophosphite of platinum; such is practically the whole list. The platinum metals have little tendency to form crystalline salts with oxy-acids, and many such salts are unquestionably incapable of existence, but in many cases at least the difficulty is our ignorance of the conditions of formation of such salts. And herein, I may say, is one of the most marked differences between investigation in organic and in inorganic chemistry. In the former the field has been so thoroughly studied that the conditions of reaction are often well known, and the course of a reaction can be foretold with considerable certainty; in inorganic chemistry the work is like exploration in an almost wholly unknown land. We know neither the possibility of existence of conjectured compounds, nor the conditions under which alone such formation or existence is possible. For this reason inorganic research is slower and far more apt to be fruitless. No better example of this can be cited than the fact already referred to, that Professor Joly, as well as myself, exhausted every method which occurred to us for the formation of the tetrachloride of ruthenium, and failed in our efforts by missing just the proper conditions, which happily Professor Antony has hit upon.

But while the platinum metals seem to form few simple salts, few or none show such a decided tendency to form double and complex salts, and this property is, to some extent, shared by the three light metals of the group.

Best known and best developed of these compounds are the cyanides, which are especially familiar to us in the prussiates of iron. In nickel we have the ordinary double cyanide, $K_2Ni(CN)_4$ or $2KCN, Ni(CN)_2$, formed by the solution of nickel cyanide in potassium cyanide. As electrolytically dissociated, the nickel is a positive ion, and the double salt is at once broken up by acids with the precipitation of nickel cyanide. The double cyanide of palladium, $K_2Pd(CN)_4$, is similar but less easily decomposed. The corresponding double cyanide of platinum, $K_2Pt(CN)_4$, is clearly a salt of the complex platinocyanic (or cyanoplatinous) acid, $H_2Pt(CN)_4$, which is formed on treating the salt with a strong acid, can be separated in a pure condition, and is an acid strong enough to expel hydrochloric acid from sal-ammoniac. The platinum atom is here a constituent of the negative ion, $Pt(CN)_4$.

If we proceed from nickel along the horizontal series, we find that while a double cobalt cyanide, $K_4Co(CN)_6$ or $4KCN, Co(CN)_2$, can be formed, it is very unstable, and belongs to the same easily decomposable class as the double nickel cyanide. This cobalt cyanide has, however, a great tendency to oxidise and form potassium cobaltcyanide, $K_3Co(CN)_6$, which is stable and a salt of the cobaltcyanic acid, which can be obtained in a free state. In passing we note a very interesting point, that under the influence of such reducing agents as potassium cyanide, potassium nitrite, and potassium sulphite, cobalt shows a great tendency to become oxidised from its bivalent condition to the very stable complex compounds in which it is trivalent; under other circumstances, simple compounds in which cobalt is trivalent are formed with great difficulty, and are of decided instability. This

seemingly anomalous property still demands an explanation.

Turning to the iron cyanides we find both types, $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, ferrocyanide and ferricyanide, well developed and extremely stable. From each, the corresponding acid can be obtained in a free state, and is a strong acid. Of the remaining metals, the double cyanide of rhodium and iridium resemble the cobaltcyanides, while of iridium the iridocyanide, $K_4Ir(CN)_6$, is also known and is stable, thus completing the analogy found in the nickel group. Potassium ruthenocyanide, $K_4Ru(CN)_6$, and osmocyane, $K_4Os(CN)_6$, resemble the ferrocyanide, the free acids being easily separable from the salts. Outside of the eighth group, the stable complex cyanides are known only in the case of manganese and chromium.

Regarding the constitution of the double cyanides, you are all familiar with the various suggestions that have been made from time to time, which involve the polymerisation, probably by threes, of the cyanogen group. To this there have been raised two objections: an explanation which is satisfactory for the double cyanides should also be available for the double chlorides, as K_2PtCl_6 , which are also salts of complex acids, and where polymerisation by threes is at least improbable; and second, it is possible to replace a single cyanogen group or chlorine atom without changing essentially the nature of the molecule, as in sodium nitroprusside, $Na_2Fe(CN)_5NO$, and potassium nitrosochlorruthenate, K_2RuCl_5NO . There is a large field for study in these cyanides from the standpoint of the newer physical chemistry.

Closely connected with the chemistry of the cyanides is that of the thiocyanates, but it has been very meagrely worked out for the eighth group. In the case of platinum both potassium platocyanate and plathiocyanates, $K_2Pt(SCN)_4$ and $K_2Pt(SCN)_6$ are known, and are salts of the platocyanic and plathiocyanic acids. These are complex acids and may be separated out, but in the free state are very unstable. The double ferric thiocyanates may be formed, but there is no corresponding complex acid, that is, they are ordinary double salts. The ferrous, cobaltous, and nickel thiocyanates are known, but form no double salts. It is extremely probable that the other metals of this group would show a full series of thiocyanates.

Another interesting class of complex salts is that of the double nitrites, first studied in the case of platinum by Nilson, but for the other platinum metals by Wolcott Gibbs, who bases upon these his method of separating the metals. More recently these nitrites have been investigated by Joly, Vèzes, and Leidé. The most familiar double nitrite is the potassium cobaltinitrite, which has long served for the separation of cobalt from nickel, and which is also used as a pigment under the name of aureolin or cobalt-yellow. These nitrites resemble, to a considerable degree, the double cyanides, and in the case of iridium the free complex iridonitrous acid has been obtained; in the case of iron, cobalt, and nickel, we have also representatives of a large class of very stable triple nitrites, first noted by Künzel and Lang, and studied by Erdmann (*J. Prakt. Chem.*, 1866, xcvi., 385). More recently these have been investigated by Przibilla (*Ztschr., Anorg. Chem.*, 1897, xv., 419), who, after great difficulty, succeeded in preparing the triple iron potassium nitrites with lead, barium, strontium, and calcium: this is the first nitrite of iron to be prepared, and leaves osmium as the only metal of the eighth group of which no nitrite is known.

In the case of all the platinum metals double sulphites are known, which are salts of complex metallo-sulphurous acids. In these metals the presence of the sulphurous acid radical cannot be detected by ordinary reagents. In the case of cobalt a full series of cobaltisulphites is known, which are stable salts, while the cobaltosulphites are very unstable. Little is known of iron and nickel sulphites, and there is much room for further investigation in the case of the sulphites of the other elements of this group.

* An Address delivered before the American Association for the Advancement of Science, New York Meeting (1900), Section C.

There is at the same time reason to believe that a study of the thiosulphites and possibly the dithionates of this group would not be without interest.

Another acid which is capable of forming complex salts is oxalic. The platoxalates are the only ones which have been carefully studied, though some work has been done upon the rhodoxalates. Several iron oxalates and double oxalates are known, but aside from this the field is unworked but promising. In this connection it may be added that while oxalic acid is the only organic acid which has been investigated to any considerable extent in complex salts, it by no means follows that it is the only acid which is capable of entering into such combinations. Some of my students have made preliminary tests with a large series of acids and found that several among them enter combination with chromium with the formation of complex salts, and it is quite possible that similar compounds may be formed with the eighth-group metals. Mention should also be made that Gibbs has introduced platinum into his complex salts, forming platinimolybdates and platininitungstates.

Since complex salts of hydrocyanic, nitrous, sulphurous, oxalic, and other analogous acids, are best developed generally with the metals of this group, it is in the study of these and other compounds of this group that we may hope to gain an insight into the constitution of these interesting compounds of which so little is known, and further extend our knowledge regarding valence, for it is just at this point that the generally accepted theory of valence begins to break down.

Before alluding to the ammonia bases, which are so well developed in this group, and would naturally follow these complex salts we have just considered, a brief digression may be made to refer to three classes of anomalous compounds, which should not be passed without reference. The first of these are the nitroso compounds. It is only recently that, largely through the efforts of Joly, the nature of the so-called nitro prussides was discovered,—double cyanides in which one cyanogen group is replaced by one nitroso group, NO. Joly then found that the old osmium acid of Fritzsche and Struve is also to be considered as a nitroso compound, and that the supposed tetrachloride of ruthenium is, in reality, a nitroso-chloride. But while there appear to be no representatives of the nitroso compounds in the cobalt or the nickel groups, several other compounds of iron are known which contain this group, as the potassium iron tetra- and heptanitrosulphonates, $K_2Fe_2(NO)_4S_2$, and $K_2Fe_4(NO)_7S_3$, and the iron nitroso-thiocarbonate and thio-antimonate of Löw. There seems also to be a nitroso-cyanide of ruthenium, corresponding to the nitroprussides, but it has not been isolated. In none of these cases has the interesting question been brought out as to whether the nitroso group remains attached to the metal when in solution, or whether it is electrolytically dissociated and acts the part of an acid radical.

In some respects yet more remarkable are the compounds formed with carbon monoxide and with phosphorus trichloride. The best known compound of this class is the nickel carbonyl, $Ni(CO)_4$, of Ludwig Mond. The nature of this volatile liquid is yet unknown, but it is by no means unique. Immediately after its discovery it was found that iron formed similar compounds, $Fe(CO)_5$ and $Fe_2(CO)_7$. That a volatile compound of iron exists had been very apparent on the lime of the Drummond light, when water-gas, compressed in iron cylinders, was used instead of hydrogen, and also in the clogging of gas burner tips with an oxide of iron, especially when a carburetted water-gas is used as an illuminant. The volatile iron carbonyl seems to be formed at ordinary temperatures by the passage of carbon monoxide through iron pipes. But it is not alone with metals that carbon monoxide combines to form volatile compounds. As early as 1868 Schützenberger (*Comptes Rendus*, 1868, lxxi., 666, 747) discovered that platinum chloride, $PtCl_2$, would combine directly with carbon monoxide, with the formation of

three distinct compounds, containing respectively one, two, and three molecules of CO to one of $PtCl_2$. A compound is also known in which one CO group replaces one cyanogen group in potassium ferricyanide, that is $K_3Fe(CN)_5CO$. This reminds us naturally of the nitroso-ferricyanide, the so-called nitroprusside. Again in 1870 Cahours and Gal (*C. R.*, 1870, lxx., 897, 1380; 1870, lxxi., 208) discovered a series of compounds containing platinum chloride united with phosphorus trichloride, and also with some of the organic phosphines. These compounds are not of the nature of double chlorides, for they can be hydrolysed with the formation of chloroplato-phosphorous acid. An analogous class of compounds of iridium has been made by Geisenheimer (*C. R.*, 1890, cx., 1004), which are also capable of hydrolysis, giving chlor-iridophosphorous acid. Geisenheimer has formed similar compounds containing bromine (*C. R.*, 1890, cxi., 40) in the place of chlorine, and also others containing arsenic (*C. R.*, 1890, cx., 1336) in the place of phosphorus. How far compounds of this nature can be extended is only conjectural, but there is evidence of the existence of something of the kind with iron.

Of binary compounds with the less negative elements, such as the phosphides and carbides of iron, little is known. Like iron, nickel and also platinum and iridium form phosphides. Iridium phosphide possesses an economic importance in that it enables the metal to be fused in a furnace. Up to the discovery of this process in 1882 by Dr. Wm. L. Dudley, the native grains of iridosmium were alone available for tipping gold pens, stylographs, and the like. It was, however, found that when iridium was heated to a high temperature in a crucible, on introducing a piece of white phosphorus, the whole mass immediately melted, and could be cast into plates, afterward to be worked up into desired form. This reminds one of the early method of working platinum by alloying it with arsenic and then roasting the arsenic off in a muffle.

There remains a single class of compounds to be noticed, the ammonia bases, whose greatest development is found in this group. The first member of this class was the compound now known from its discoverer as the green salt of Magnus, which was first made in 1828 (*Ann. der Phys.*, Pogg., 1828, xiv., 239). Then came the work of Gros, of Reiset, and of Peyrone. Among the many chemists who have cultivated this field are Clève, Jörgensen, who has given us most of our knowledge of the rhodium bases, Gibbs, Palmaer, who has developed the iridium bases, and Joly, who has revised the bases of ruthenium; while the theory of these bases has been discussed especially by Claus, Blomstrand, Jörgensen, and Werner. In connection with these bases, appear what must with our present knowledge be considered anomalies. The greatest development of these bases is found with platinum, where nearly or quite a dozen distinct classes of bases are known, and where we find several groups of isomers, which Werner seeks to explain as stereoisomers, while Jörgensen strenuously combats the view. In type, the palladium bases resemble those of platinum, but as far as yet studied are much less well developed. Nickel, on the other hand, forms no true bases, though many ammonia compounds. The cobalt, rhodium, and iridium bases are all formed on the same general types, but by far the greatest development is found in cobalt, which almost rivals platinum in the number of classes; but few of these are developed with iridium, and fewer still with rhodium. In the iron group no bases are formed by iron, and only two or three ammonia compounds; ruthenium and osmium form fewer bases, as far as yet investigated, than any of the other platinum metals. It is interesting to note, however, that one of these ruthenium bases, discovered by Joly, which possesses intense tinctorial power, resembles very strongly an organic dye, both on fabrics and as a stain in microscopy. The constitution of the ammonia bases is to-day, as it has been for half a century, one of the greatest problems of inorganic chemistry, and it is apparently no

nearer solution. In accordance with the valence theory, it becomes necessary with Jørgensen to assume the existence of chains of at least four NH_3 groups in a molecule, stable enough to be unaffected by aqua regia, and also that these ammonia groups are replaceable by water molecules. We must also assume that while in ordinary salts, as, for example chlorides, the chlorine atoms, which are directly united with the metal, are dissociated in aqueous solution, in these bases the chlorine which is directly united with the metal is not dissociated, but that which is united with the metal through the medium of one to four ammonia groups is dissociated. Led by a consideration of these seeming inconsistencies, Werner has proposed his theory of co-ordinated groups within the molecules,—a theory which seems to possess at least elements of truth, even if not expressing the whole truth. It is possible, too, that Werner's theory may explain some of the difficulties of the theory of electrolytic dissociation, and harmonise it with the hydrate theory of solution.

The constitution is, however, not the only problem of these bases. To my mind their connection, or rather lack of connection, with the periodic system, is one of the most inexplicable facts in chemistry. It makes it apparent that while the periodic law expresses a truth, without doubt the greatest generalisation of modern chemistry, yet even this is in its present statement not the whole truth. We find a marvellously full development of these bases in connection with cobalt, platinum, and chromium. Manganese and iron which lie between chromium and cobalt form no bases. The higher members of the chromium group—that is, molybdenum, tungsten, and uranium—form no bases, while the higher members of the iron series—that is, ruthenium and osmium—do. Of nickel, which stands next to cobalt and resembles it so closely, no bases are known, and yet it is the lowest member of the series which contains platinum. It is true that bivalent cobalt forms perhaps, like nickel, no bases, but as trivalent cobalt forms so many bases, trivalent iron would seem likely to form many, instead of none. If indeed manganese and iron are capable of forming these bases, it seems strange that no one has yet happened upon the proper conditions. It is the consideration of a subject like that of these inorganic bases which forces upon us a realisation of how much there is after all which we do not know about chemistry.

We turn now to a short consideration of the eighth group from a theoretical standpoint. Following Dr. Venable (see Periodic Table, p. 16) we may assume that each of the first seven groups consists of a group element, as in group one, lithium; a type element, as sodium; and two series, one of more positive elements, as potassium, rubidium, and caesium, and the other more negative, as copper, silver, and gold. Further, the more positive the type metal, the more closely will the metals of the positive series resemble it; the more negative the type metal, the more closely will the negative series resemble it. Thus in the first group, the positive series potassium, rubidium, and caesium closely resembles the type element sodium; in the seventh group the negative series, bromine and iodine, resembles the type element chlorine. Now the eighth group differs materially from the other seven in that it contains three series, with no group or type element. These three series are transitional from the least positive among the seven positive series, manganese, to the least negative among the negative series, copper, silver, and gold. The properties of the metals of group eight show this transition as from a chemical standpoint; iron, cobalt, and nickel form a direct gradation between manganese and copper. Now comes a further question as to possible transition elements between the most negative series, fluorine, chlorine, bromine, iodine, and the most positive series, sodium, potassium, rubidium, and caesium. From a theoretical standpoint such transition elements should be neither positive nor negative, and should have a valence of zero. A few years ago the realisation of such a conclusion would have seemed impossible, yet,

since the discovery of argon and its congeners, it seems almost probable that these places have been filled in accordance with theory. If we take the most generally accepted atomic weights, we find helium preceding lithium, neon following fluorine and preceding sodium, and argon really between chlorine and potassium, but with an atomic weight apparently slightly greater than that of potassium which follows it, resembling in this respect cobalt and nickel of this same group, and also tellurium and iodine. There would, in addition, be expected from the analogies of group eight, one, two, or three transitional elements between bromine and rubidium, of atomic weight 80 to 85, and Ramsay has suggested that krypton may belong in this place—so also an element or elements of similar character might be expected between iodine and caesium, with atomic weight of about 130. The recently published work of Ladenburg and Kruegel on krypton give it an atomic weight of about 59. This would, as Professor Ladenburg suggests, make it immediately precede copper; but unless we change very materially our ideas of the periodic law, it is difficult to conceive of an element with the properties of krypton lying between nickel and copper. If these inert gases belong in the eighth group it may seem strange that iron and the other familiar metals which belong here should be so unlike such a type element as argon or neon; it must, however, be borne in mind that this is only an expected exaggeration of the departures found in the first and seventh groups, where copper departs from its type element sodium, and manganese from its type element chlorine. As to whether three elements are to be expected of atomic weight 150 between the light and the heavy platinum metals, we have little data upon which to theorise. As a matter of fact there is very little definite knowledge of the elements between cerium and tantalum. The inter-Jovian planet proved to be an indefinitely large number of asteroids; Sir William Crookes's study of the rare earths leads him to the conception of a group of asteroidal meta-elements in this vacant space in the periodic table. We must await further knowledge before these problems can be satisfactorily solved.

In conclusion, one word as to a very practical problem connected with this group. It is but a few years past a century since the use of platinum was introduced into the chemical laboratory. For a few decades the supply exceeded the demand, but the applications of platinum have steadily increased, and never so rapidly as in the last two decades. For many purposes no substitute for platinum has been found. At the same time the supply of platinum is not keeping pace with the demand, and as a result the price of platinum has very materially advanced. While platinum is very widely distributed, there are few places where it occurs in workable quantities. It is possible, however, that it has been often overlooked, as in placer mining for gold, and efforts have been made to attract miners' attention to more careful search for platinum deposits. At the present outlook it will, within a few years, be imperatively necessary either to materially increase the platinum supply of the world or to replace it for many purposes by some other substance. How this problem will be solved cannot now be foreseen.

On Lilienfeld's Synthetic Peptone.—M. Klimmer.—Lilienfeld has prepared a substance which he considers to be peptone, by the condensation of phenol and glycol by means of oxychloride of phosphorus, or by the condensation of asparagin and para-amidobenzoic acid in the presence of glacial phosphoric acid or metaphosphoric acid, &c. In taking up this subject M. Klimmer has shown that Lilienfeld's conclusions are incorrect; in fact, the substance obtained differs from peptone in at least two characteristics, it does not show the biuret reaction, and it decomposes with the greatest ease into its constituents.—*Pflüger's Archiv*, vol. lxxvii, p. 210.

THE
ESTIMATION OF PHOSPHORUS IN STEEL, &c.

By FRED IBBOTSON and HARRY BREARLEY.

A BEWILDERING number of papers have been written on the estimation of phosphorus in steel. The following process is described only because it is believed to be quite new in respect to the means of estimating the phosphorus.

In iron and steel works phosphorus is almost exclusively separated as ammonium-phosphomolybdate. Mainly for the sake of dispatch, it is either weighed in that form, or the MoO_3 estimated volumetrically after reducing with zinc, or by saturating with standard alkali.

The percentage of phosphorus in the yellow precipitate, says Blair, is given by various authorities from 1.27 to 1.75. Both Blair ("Chem. Anal. of Iron," 2nd edition, 1891)* and Clowes and Coleman ("Quant. Anal.") give the formula $(\text{NH}_4)_3\text{PO}_4 \cdot 11\text{MoO}_3$ to the precipitate dried at 120°C .; Arnold ("Steel Works Analysis") gives the same formula plus nine molecules of water when dried at 100°C ., and each compound is said to contain 1.63 per cent P. Really the formula $(\text{NH}_4)_3\text{PO}_4 \cdot 11\text{MoO}_3$ corresponds to 1.79 per cent P.

Hundeshagen (CHEM. NEWS, lx, 168)—who has made the most complete examination of the formation of the yellow precipitate we have seen—and many others write the formula $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ when the precipitate is dried at 120 – 150°C . This formula has been adopted in the calculations of the following process.

It has been previously shown (CHEM. NEWS, lxxix, 4) that if we add to a solution containing Mo and P enough HCl to prevent the formation of a precipitate, on adding at least enough lead acetate to combine with the molybdic and phosphoric acids as PbMoO_4 and PbHPO_4 , and then add this heated mixture to another containing ammonium chloride and at least enough ammonium acetate to decompose the free HCl, we get PbMoO_4 precipitated and PbHPO_4 in solution. The results are exact when much greater proportions of P than P : 12MoO_3 are present. The new process depends on these facts.

Various amounts of dried yellow precipitates prepared from soda phosphate were treated in the way indicated. The results were:—

Grm. P calculated from—	
$(\text{NH}_4)_3\text{PO}_4 : 12\text{MoO}_3$.	PbMoO_4 .
0.00041	0.00039
0.00082	0.00082
0.00164	0.00163
0.00246	0.00247
0.00410	0.00393

An outline of the process applied to steels is as follows:—Dissolve 2 grms. of the sample in 45 c.c. 1.20HNO_3 ; add permanganate until a pink colour or an MnO_2 precipitate persists after a few minutes' boiling; clear with FeSO_4 , add about 4 c.c. strong ammonia, and then to the clear hot solution 30 c.c. of the molybdate reagent. Shake the stoppered flask, allow to stand a few minutes at 70 – 80°C .; pass through small pulp filter, wash, dissolve off yellow precipitate with a few drops of ammonia, clearing the sides of the flask with the same solution as it drops from the end of the funnel; pass solution again through the filter into a small beaker (200 c.c.), and wash. Add 10–12 c.c. HCl, 10 c.c. lead acetate (40 grms. per litre), and heat. In the washed-out flask heat a mixture of ammonium chloride (= 10–12 grms. $(\text{NH}_4)\text{Cl}$) and 50 c.c. strong ammonium acetate; mix the

two solutions in the flask with shaking, filter, and weigh as PbMoO_4 . The weight multiplied by 0.007 gives the weight of P in the steel. The operation is very conveniently performed with batches of four, which are completed in an hour and a half. A single estimation takes about forty minutes.

Some noteworthy features of the process are:—The PbMoO_4 is quite insoluble in the solutions used; being very granular it filters readily; it can be ignited speedily without loss of weight, and it weighs more than one hundred and forty times heavier than the phosphorus to be estimated.

Although it simplifies the process to use constant amounts of reagents, still some variation is possible without greatly sacrificing accuracy. For instance, a series of two separate steels were in each case dissolved in 45 c.c. HNO_3 , but varying amounts of strong ammonia were added, and the process concluded as usual. The results were—

$(\text{NH}_4)\text{HO}$.	Per cent P.	
	I.	II.
0	0.088	0.032
2	0.090	0.032
4	0.090	0.034
6	0.089	0.034
8	0.091	—



The process has been satisfactorily applied to the estimation of phosphorus in pig-irons, nickel-steel and alloys, chrome-steels, tungsten-steels, spiegeles, and ferromanganese. The graphite of pig-iron should be filtered off before adding the permanganate. Chrome-steels require more permanganate, because the Cr is oxidised to CrO_3 and de-oxidised by the FeSO_4 . Spiegeles, FeMn, and tungsten steels also need more permanganate. Very little WO_3 is precipitated during the oxidation; it is well, however, to pass through a filter before adding the molybdate. A little WO_3 is sometimes precipitated with the phospho-molybdate, and gets weighed finally as PbWO_4 , but in extreme cases it influences the result only to about 0.002 per cent P. It is detected by dissolving the lead molybdate in a few c.c. HCl, evaporating, and taking up with dilute HCl. The WO_3 remains undissolved.

As it is important that no MoO_3 , deposited from the reagent or dried on the neck of the bottle, should pass into the solution of the sample, the ammonium molybdate is filtered as required through asbestos felt arranged in the throat of a stopcocked cylinder funnel, as shown in the sketch.

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* In 1895 Blair and Whitfield (Journ. Am. Chem. Soc., xvii, 747), after analysing ten different samples of the yellow precipitate, fixed 1.794 as the ratio—

$$\frac{\text{P}}{100\text{MoO}_3}$$

which agrees with the ratio calculated from Hundeshagen's formula.

LABORATORY APPARATUS.

A STEAM-PIPE CONDENSER AND A GLASS TUBE OVEN.

By F. W. STREATFEILD, F.I.C.,
and
F. SOUTHERDEN, F.I.C.

FIG. 1 shows the first piece of apparatus as set up for work in the laboratory. It is intended for the distillation of substances which tend to solidify in the condenser. To obviate this, a glass tube runs the whole length inside, and is connected to the steam generator by a rubber tube and pinchcock. When a block threatens, the cock is opened and the heat from the steam rapidly removes any obstruction.

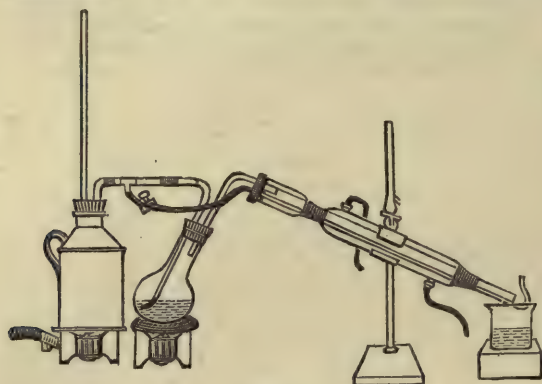


FIG. 1.

This method is quicker and more under control than the ordinary one of letting the water out of the condenser. It is necessary that the condenser should possess a wide mouth, so that the two tubes may be readily inserted.

Before proceeding to make a determination of the melting-point of an organic compound, it is most essential that any adhering solvent which may have been used in its purification be removed. This may be effected by placing the substance in the water- or air-oven. If the drying is conducted in a current of hot air, the operation of complete drying is more quickly carried out. The little contrivance seen in Fig. 2 is for this purpose.

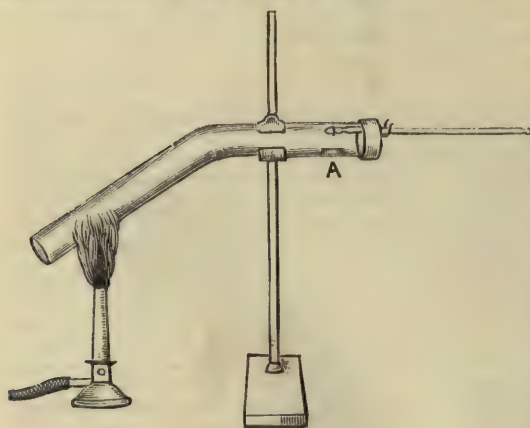


FIG. 2.

A piece of combustion tube about 35 c.m. in length and 18 m.m. internal diameter is bent, as shown, at an angle of 140° . It is clamped with the shorter arm nearly horizontal, and in this is placed the substance (at A) on a small piece of drying paper. A wire is twisted round the

short arm and bent over the end to form a loop, through which passes a thermometer, the bulb being over the sample. The thermometer maintains its position by its own weight, but to prevent actual contact with the glass tube a piece of fibrous asbestos is wrapped round the bulb. If this is done with wet asbestos no difficulty will be encountered in making it adhere. The substance is dried by a current of hot air produced by the Bunsen burner. This may be placed at any height and at any point along the longer arm, the temperature varying accordingly.

The principal features of the apparatus are that the range of temperature is practically unlimited, and that, without any precautions, the thermometer readings may be kept constant within a few degrees.

With a tube of the above dimensions, the thermometer will always be 10° or 15° higher than the substance, so that the temperature may be safely maintained at its melting-point without fear of melting actually occurring.

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Finsbury.

ON THE
COMPOSITION OF N. S. WALES LABRADORITE
AND TOPAZES, WITH A COMPARISON OF
METHODS FOR THE ESTIMATION OF
FLUORINE.*

By G. HARKER, B.Sc.

Analysis of Mineral Labradorite from N. S. Wales.

THE specimen described in the following note was collected by Mr. D. A. Porter, of Tamworth, on Sandilands Mountain, some 57 miles from Tenterfield, who forwarded it to Professor Liversidge for examination. Mr. Porter states that it occurs there in a basalt, and also between Hillgrove and Grafton.

The specimens were in broken fragments about half an inch in diameter. Some were colourless, others brown to greyish. One perfect cleavage was exhibited, probably basal, and a second not quite so good. The fracture was uneven, inclining to conchoidal; the lustre vitreous. The hardness was 6 and the sp. gr. 2.70. Before the blowpipe it fused to a colourless glass, its fusibility being about 3. All these properties agree in every detail with those given in Dana for typical labradorite, as do all the optical properties which were determined. The refractive index was low and the double refraction weak. In convergent polarised light a cleavage flake gave a figure with one brush nearly straight, and was therefore the section of a bi-axial mineral cut at right angles to the optic axis, the optic axes being nearly at right angles. The dispersion could not be obtained. The mineral was optically positive and showed multiple twinning.

Analysis.

	1.	2.	3.	4.	5.
	New South Wales.	Veltlin.	Thann- berghthal.	Ramen- Brod.	
Silica	55.05	54.81	55.15	53.61	54.55
Alumina	29.70	29.70	29.15	29.68	28.68
Ferric oxide ..	30.15	0.42	—	—	1.03
Lime	10.32	9.61	9.90	10.96	11.23
Soda	5.11	Undeter.	5.23	4.36	4.62
K ₂ O	None	0.29	0.80	1.15	0.42
MgO	None	0.28	—	—	—
H ₂ O on ignition	Undeter.	0.13	0.67	0.65	—
	100.63	Incompl.	100.90	100.41	100.53

Nos. 1 and 2 are analyses of two different samples of the mineral. In the first analysis the ferric oxide was

* Read before the Royal Society of N. S. Wales, December 6, 1899.

not determined separately; 30·15 is the percentage of mixed oxides of iron and alumina; the analysis was done on the dried ignited sample. Nos. 3, 4, and 5 are three analyses of labradorite given in Dana, and are put in for sake of comparison. The silica in the labradorite analyses given in Dana varies from 52·45 to 56·18, the alumina from 27·33 to 29·85, the lime from 9·90 to 12·01, and the soda from 3·90 to 5·23. From these it will be seen that the chemical composition of the mineral agrees well with that of labradorite, and taken in conjunction with its physical properties shows that it is that mineral.

Topaz.

The following investigation was also made in the Chemical Laboratory of the University of Sydney at the suggestion and under the direction of Professor Liversidge, with the object of determining the composition of some N. S. Wales specimens, and of comparing certain of the published methods for the analysis of fluorides. The most difficult constituent to analyse in topaz is fluorine, for the estimation of which a number of methods have been proposed. To find the most satisfactory was the first object in view.

Before proceeding farther a *resumé* of previous methods for the determination of fluorine might be of use:—

(a) *Fluorides not decomposable by Sulphuric Acid.*—Berzelius was the first to accomplish the analysis of fluorides undecomposable by sulphuric acid. He fused the fluorides with alkaline carbonates. To separate the silica from silicates combined with fluorine he employed a solution of zinc carbonate in ammonia; zinc silicate is formed, and the solution is freed from the rest of the zinc oxide by evaporation.

H. Rose in 1849 separated the fluorine as calcium fluoride, a more convenient form than the sodium fluoride employed by Berzelius. He precipitated the calcium fluoride together with calcium carbonate to help in its filtration. He pointed out that some fluorides which were not associated with silica were not completely decomposed by fusion with alkaline carbonates. A combination of the methods of Berzelius and Rose is still the best method known for the estimation of fluorine. Wöhler in analysing topaz fused with sodium carbonate alone.

(b) *Fluorides decomposable by Sulphuric Acid.*—For the analysis of these a large number of methods have been proposed; Wöhler added silica and sulphuric acid, weighed, and determined the fluorine by loss due to escape of silicon tetra-fluoride.

Liversidge (CHEMICAL NEWS, 1871) decomposed with silica and sulphuric acid, and collected the silicon tetra-fluoride in ammonia solution. By partial evaporation the gelatinous silica was dissolved. He then added potassium chloride, and weighed the fluorine directly as potassium silicon fluoride.

1872, Fresenius collected the silicon tetra fluoride in tubes containing moistened pumice.

Penfield (*Journ. Chem. Soc.*, 1879) passed the silicon tetra fluoride into a solution of potassium chloride and alcohol, and titrated the hydrochloric acid set free by the reaction.

Carnot (*Comptes Rendus*, 1893) collected the silicon tetra fluoride in a 10 per cent solution of potassium fluoride, and weighed as potassium silicon fluoride.

Three of the above methods were tried for the estimation of fluorine in topaz:—

First Method, Fusion with Alkaline Carbonates.—The topaz first analysed was from Mudgee, N.S.W. It was in the form of transparent rolled pebbles of from one-quarter to one-eighth of an inch in diameter. The method of analysis first used was that of Wöhler, as given in his "Mineral Analysis," English edition of 1871.

"The substance, when fused with four times its weight of anhydrous carbonate of soda, is decomposed with formation of fluoride of sodium, which is extracted with water. Before filtering off the residual silicate of alumina, the

solution should be digested with carbonate of ammonia to precipitate any small quantities of alumina and silica which may have been dissolved." The residue is evaporated down with hydrochloric acid, and the silica and alumina extracted. The fluorine in solution is removed as calcium fluoride by adding calcium chloride.

This method, when tried on the topaz crystals from Mudgee, gave results for fluorine which were low and irregular, viz., from 5 to 11 per cent. On treating some Brazilian topaz later in the same way, similar unsatisfactory results were obtained, viz., 4·7 to 12·9 per cent.

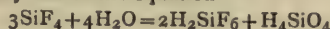
Second or Tetra-fluoride Method.—That of Liversidge as given in Crookes's "Select Methods," p. 580, 1884 edition.

In this method the substance is decomposed with sulphuric acid and silica, and the silicon tetra-fluoride passed into solution of ammonia. The mixture is heated in a platinum retort, first over the water-bath and finally at 160° C., the last traces of gas being removed by a current of air. The ammonia solution is evaporated until the gelatinous silica passes into solution, and is then precipitated as potassium silicon fluoride by potassium chloride and alcohol.

So far this method had only been used for the determination of fluorine in coprolites and apatite. In order to make the method applicable to topaz, which is not decomposable by sulphuric acid, the topaz was first fused with sodium potassium carbonate, silica was then added, and the mixture decomposed with sulphuric acid.

Preliminary trials were made with calcium fluoride, apatite, and cryolite, the substance in each case being fused with 2 or 3 grms. of sodium potassium carbonate and then decomposed. The silicon tetra-fluoride was collected in water after the first few experiments, as it was found that on evaporation with ammonia some of the hydrogen silicon fluoride was converted into silica. The method gave uniform results, which, however, were rather low in all cases.

The cause of the lowness in the results is not apparent. It is probably due to the equation—



not being a quantitative one. Potassium silicon fluoride was found to be slightly soluble in a 50 per cent solution of alcohol. After filtering off the gelatinous silica, the solution in which the potassium silicon fluoride was precipitated was always made of the same volume, and hence the error due to solubility could be allowed for. Potassium chloride was used prepared from different sources, but caused no difference in the results.

The discrepancy was not due to incomplete absorption of silicon tetra-fluoride in the water. A second absorption-tube gave no trace of a precipitate. To completely remove the gas from the decomposition flask, dry air was passed through for four to five hours.

The amounts of calcium fluoride used were varied to see if the error was constant or proportional. The percentage of fluorine obtained was increased as more calcium fluoride was taken, but not proportionally, and tended to reach a maximum. For amounts approximately equal the results were constant, and hence the error can be corrected from the weight of potassium silicon fluoride obtained.

(To be continued.)

Synthesis of *aa*-Dimethyl- γ -cyanotricarballylic Ether and *aa*-Dimethyltricarballic Acid.—A. Haller and G. Blanc.—*aa*-Dimethyltricarballic acid, $\text{C}_8\text{H}_{12}\text{O}_6$, is one of the numerous products of degradation which are obtained as a result of oxidation of certain terpenic derivatives, in particular those which are allied to pinene and camphene. The synthesis of this substance therefore presents a certain importance from the point of view of the determination of constitutional formulæ in this series. —*Comptes Rendus*, cxxxi., No. 1.

CORRESPONDENCE.

THERMAL CENTRES OF STABILITY.

To the Editor of the Chemical News.

SIR,—It appears that a confusion has arisen in regard to the sense in which I have used the words "heat of formation." It is certainly not a good term, as it does not express clearly the idea of elevation or degradation of the potential energy which usually accompanies the change of one system into another.

The following, I think, should make my meaning clear:—Imagine a chemical system A. Let the absolute amount of energy contained in it at T° and at constant volume be E_A . Now, suppose by some means the system A is converted isothermally into another system B; the volume remaining constant. Let the quantity of energy which must be either supplied to, or abstracted from, the system A in order to convert it into B be denoted by $\pm q$. Then—

$$E_A \pm q = E_B,$$

or—

$$\pm q = E_B - E_A.$$

Here q denotes what I have called the "heat of formation." It is simply the energy that must be supplied to one system to "form" the other system from it; q is negative or positive, according as $E_B \leq E_A$. The term "negative heat of formation," if used merely to express the degradation of potential energy brought about by the change, becomes intelligible.

As Mr. Hill points out, if used in an absolute sense, it becomes incomprehensible. Mr. Hill's suggestion that for "negative heat of formation" the term "minimum heat of formation" be substituted, would bring out the nature of the physical changes involved very clearly. In the mathematical treatment of the subject, however, we only deal with the elevation or degradation of energy. It would perhaps be better to avoid the term "heat of formation" altogether, and use "heat of reaction" or "heat toning."—I am, &c.,

GEOFFREY MARTIN.

13, Hampton Road, Bristol.

THE ACTION OF IRON ON WATER.

To the Editor of the Chemical News.

SIR,—It seems to me astonishing that our modern standard text-books on chemistry do not mention the fact of the readiness with which ordinary iron decomposes water at ordinary temperatures with an evolution of hydrogen gas. In our elementary work here, when studying the effect of water on metals, it is always a source of much interest to observe from day to day the continued effect of water on the commoner metals. In the case of iron, when a test-tube of filings is covered with water, "red-rust" first occurs on the surface, and then beneath this rust appears the greenish-black oxide in a flocculent form (this is referred to later on), and finally, bubbles of hydrogen. By suitably arranging an apparatus, a volume of gas may be collected in two weeks, using iron filings, or in a few hours if *ferrum reductum*, B.P., be used, sufficient to demonstrate its properties. The same is true if zinc dust be used. Distilled water recently boiled and cooled, I find shows an evolution of hydrogen sooner than common water, and no trace of red rust is observed if air be excluded.

The experiment, lasting as it does over a fairly long interval of time, centres an interest which is so often lost in those of a shorter duration, and it seems to me most instructive, especially when afterwards taken in conjunction with the action of sodium on water.

Although numbers of papers have appeared on the

above subject, both in English and German, yet our modern English text-books pass it over, and also the fact that the oxide first formed contains ferrous iron. This was shown to be the case by Liversedge (*CHEM. NEWS*, lxi., p. 230).

Many experiments have been carried out here quite recently, using different grades of iron and various waters, but I find most of the results have already appeared in German papers.

Many teachers I have spoken to on the subject seemed to be quite unaware of the fact that hydrogen gas was evolved at ordinary temperatures, most of the books either stating there is no action, or that the gas is slowly evolved at 100° .—I am, &c.,

WM. FRENCH.

Bury Grammar School.
July 21, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 1, July 2, 1900.

The Combustible Gases of the Air. Air in Woods, Air on High Mountains.—Armand Gautier.—The author continues his researches on the proportion of hydrogen and the combustible hydrocarbons in the air. His experiments were conducted in a wood containing oak, pine, and birch trees at Lainville. He found that the air still contains both hydrocarbons and hydrogen. In order to answer the question as to whether these are necessary constituents of the atmosphere or whether they disappear in very pure air, he continued his researches on Mount Canigou, in the Pyrenees, at a height of 2785 metres. He then finds that the proportion $\frac{C}{H}$, i.e., of carbon to com-

combustible hydrogen, which was 3.49 in the air of Paris, and 2.2 in the air of woods, falls to 0.33 on the high mountain; thus showing that, in proportion as we rise in the air, away from the region of human industry and animal life, and also from the region of damp and vegetation, the hydrocarbons in the atmosphere tend to disappear.

The True Atomic Weights of Ten Elements deduced from Recent Work.—G. Hinrichs.—The results of various authors are discussed with regard to the atomic weights of hydrogen, carbon, oxygen, chlorine, bromine, sulphur, sodium, silver, barium, and boron.

A General Theory of Acidity.—M. de Forcrand.—The author's theory, at present very incomplete, appears to account for the greater quantity of organic and mineral compounds whose acidity is well known, from values which correspond in a remarkable manner with those given by experiment. The number of facts quoted is too great for the supposition of mere coincidence to hold good. When the theory is more fully developed, it will furnish a means of predicting the acidity of a hydrogen compound whose constitutional formula is known.

Hydrogenation of Acetylene and of Ethylene in presence of Platinum Black.—Paul Sabatier and J. B. Senderens.—The authors find that platinum black only induces the hydrogenation of ethylene when hot, whilst the hydrogenation of acetylene can take place in the cold after a considerable lapse of time.

Methoxyhydratropic Acid obtained by Oxidation of Anethol. Identity of Phloretic Acid and Hydroparacoumaric Acid.—J. Bougault.—In a preceding paper, the author showed that the oxidation of anethol

by iodine and yellow oxide of mercury gives an aldehyde of formula $C_{10}H_{12}O_2$, and that the oxidation of this aldehyde by silver oxide furnishes an acid of formula $C_{10}H_{12}O_3$ or $CH_3O-C_6H_4-C_2H_4-COOH$, and that this acid constitutes, with methylphloretic and methylhydroparacumaric acids, an isomeric series. Whilst examining the properties of these two latter acids, the author was struck by their similarity, and has since proved them to be identical.

Methods of Synthesising the Higher Homologues of Acetylacetic Ether and Acetylacetone.—L. Bouveault.—Method of formation of the compounds $C_2H_2(Cu_2Cl_2)_2KCl$ and $C_2H_2[(Cu_2Cl_2)_2KCl]_2$. This paper gives an account of the continuation of the work recently published on the transformation of yellow and colourless crystals corresponding to the above formulæ from one into the other.

Metallic Compounds of Diazoamidobenzene.—Louis Meunier.—The author prepares and examines the properties of the copper derivative of diazoamidobenzene, and also of the chlorhydrate, bromhydrate, and iodhydrate of the same derivative.

Action of Nitric Acid on Trichlorogaiacol.—H. Cousin.—The author finds that nitric acid acts on trichlorogaiacol, giving a body which is at the same time a product of oxidation and of condensation.

The Aloines.—E. Léger.—An account of the various derivatives of the aloines, their mode of preparation and their properties, are given in this paper.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 5.

Mathematical Laws of Chemical Equilibria.—O. Boudouard.—Already noticed in this column.

New Absorber-washer for Gas.—A. Gautier.—This absorber is made entirely of glass, and consists essentially of two bulbs of as near as possible the same capacity—that is, about 10 c.c.—connected by means of a wide vertical tube 10 or 12 c.m. in length, and also by a narrow bore serpentine tube surrounding the first-named one. At its lower extremity the central tube penetrates the lower bulb, to which it is fused, the end nearly reaching to the bottom of the bulb. The small serpentine tube starts from the middle of the side of the lower bulb, passes round and round the central tube, and joins the centre of the side of the upper bulb, to which it is fused; this latter terminates in a tube closed with a ground-glass cap and a side tube serving for the escape of the gas. To use this apparatus, the lower bulb is completely filled with the absorbent liquid (sulphuric acid mixed with anhydride, for example, if ethylene is to be absorbed), and the gaseous mixture is passed into the bulb through another tube joined into its upper side. The gas entering by this tube gradually fills the upper part of the bulb, forcing the liquid through the serpentine tube, by which it passes to the upper bulb, whence it again falls into the lower one through the central tube. At a given moment, however, the gas level reaches the level of the serpentine, and then, owing to a slight contraction in this tube which checks the flow, passes in bubbles up the serpentine. Arriving at the upper end of this tube, the gas escapes into the upper bulb, while the partly used liquid passes to the lower part of the lower bulb. In this manner the following triple result is attained:—(1) The gas is washed in the state of as small bubbles as may be desired; (2) the absorbent liquid is constantly being circulated and renewed; (3) The gas is washed with a minimum amount of absorbent liquid. With this apparatus, containing only 8 c.c. of potash of $d = 1.3$, we have washed and absorbed all the carbonic acid from 200 litres of air.

Analysis of Water from Jouhe.—P. Bourcet.—Already inserted.

Remarks on the Cryoscopy of Rhamnose and Rhamnitronic Acid of M. Tanret.—M. Ponsot.—The recent measurements made by M. Tanret on rhamnose and rhamnitronic acid furnish us with two fresh examples of a coefficient of falling temperature very variable with the concentration. In most chemical work, when cryoscopy is used to decide between two figures for a molecular weight, one determination only is made, or the results of a single determination is given with a fall of about 1° ; this, the author thinks, is quite illusory.

Sulphides of Molybdenum.—M. Guichard.—Already noticed in this column.

Production of Crystallised Salts of Bismuth.—A. de Schulten.

Production of Iodised Carnallites of Potassium and Ammonium.—A. de Schulten.

Production of Vanadinites of Cadmium.—A. de Schulten.—These three articles have appeared in full.

Synthesis of Derivatives of Cyclopentane by the Use of Adipate of Ethyl. (II.). Total Synthesis of the Phorone of Camphoric Acid.—L. Bouveault.—Already noticed.

Camphenylone.—E. E. Blaise and G. Blanc.—Already noticed.

Dinitration of Safranin.—G. F. Jaubert.—Already noticed.

Modifications undergone by Essence of Lavender during Vegetation.—E. Charabot.—The author finds that, as in the case of essence of bergamot, etherification is accompanied by a diminution of the total amount of alcohol and of free acids. These facts allow of the conclusion that here again the ethers take rise from the direct action of the acids on the alcohols. Under these conditions, during the development of the plant, one part of the linalol is etherified, while another part of this terpenic alcohol becomes dehydrated. On the other hand, as soon as the etherification is finished—which takes place when the plant is on its decline—we notice a fairly considerable increase in the richness of the essence in alcohol.

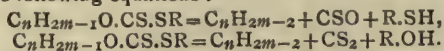
Remarks on the Metamorphoses and the Migrations of the Compounds of the Linalol Group in Plants.—E. Charabot.—The author has shown that linalol is first transformed during the growth of plants partly into ether and partly into terpenes. Essence of orange leaves contain a considerable proportion of acetic ethers of linalol and geraniol (about 60 per cent), as well as free linalol and geraniol (20 to 25 per cent). In the flower the proportion of geraniol with regard to linalol seems to have increased. When finally the essence becomes localised in the orange skin, the proportion of limonene becomes considerable, while the alcohols have almost entirely disappeared; the linalol has given limonene by dehydration in the parts where chloro-vaporisation takes place actively, and the geraniol is converted into citral in the organs which energetically fix oxygen.

MISCELLANEOUS.

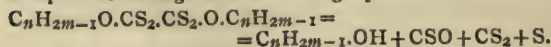
Institute of Chemistry Examinations.—Pass Lists (July, 1900).—*Intermediate Examination:* J. A. Brown, Univ. Coll., Nottingham; E. M. Chapman, Pharmaceutical Society's Laboratories, and King's Coll., London; F. Cunliffe, Owens Coll., Manchester; J. A. Dewhurst, Yorkshire Coll., Leeds, and Pharmaceutical Society's Laboratories; W. D. Dick, King's Coll., London; A. W. Ellis, Mason Univ. Coll., Birmingham; A. Gray, Glasgow and W. of Scotland Tech. Coll.; J. E. Jenkins, King's Coll., London; W. Lowson, Yorkshire Coll., Leeds; W. W. Lumsden, Glasgow and W. of Scotland Tech. Coll.; B. G. McLellan, Glasgow and W. of Scot-

land Tech. Coll.; W. H. Nuttall, Univ. Coll., Nottingham; W. Partridge, Finsbury Tech. Coll., London; S. O. Richmond, Finsbury Tech. Coll., London; A. J. Robertson, Univ. Coll., Dundee, and under R. R. Tatlock, Esq., F.I.C.; P. W. Tainsh, Glasgow and W. of Scotland Tech. Coll.; W. S. Tebb, M.A., M.D. (Cantab.), Cambridge University, and King's Coll., London; J. Thorburn, Glasgow and W. of Scotland Tech. Coll.; F. W. Watson, Glasgow and W. of Scotland Tech. Coll. *General Practical Examination*: *A. Scott, Glasgow Univ., Glasgow and W. of Scotland Tech. Coll., and under R. R. Tatlock, Esq., F.I.C. *Final A.I.C. Examination*:—*In Mineral Chemistry*: A. Baguley, B.Sc. (Wales), Univ. Coll., Bangor; A. Davidson, Glasgow and W. of Scotland Tech. Coll.; *T. Hartley, Yorkshire Coll., Leeds; H. W. Kinnersley, Merchant Venturers' Tech. Coll., Bristol, King's Coll., London, and under E. H. Cook, Esq., D.Sc. (Lond.), F.I.C.; O. Reinherz, B.A. (Cantab.), Trinity Coll., Cambridge. *In Metallurgical Chemistry*: A. G. Levy, Finsbury Tech. Coll., London; *J. J. Morgan, of Wednesbury. *In Physical Chemistry*: T. H. Pope, A.C.G.I., City and Guilds of London Institute, Central Institution, and Finsbury Tech. Coll., London. *In Organic Chemistry*: F. G. H. Billows, A.C.G.I., City and Guilds of London Institute, Central Institution, and Finsbury Tech. Coll., London. *In the Analysis of Food and Drugs, including an Examination in Therapeutics, Pharmacology, and Microscopy*: S. Aston, Univ. Coll., London; N. P. Booth, Mason Univ. Coll., Birmingham; *T. W. Glass, B.Sc. (Lond.), Pharmaceutical Society's Laboratories, and under Messrs. T. H. Redwood and A. J. de Hailes, F.F.I.C.; W. H. Jollyman, Finsbury Tech. Coll.; *W. N. Platt, B.Sc. (Lond.), A.R.C.Sc. (Lond.), Royal Coll. of Science, London; *S. A. Woodhead, B.Sc. (Dun.), Durham College of Science, Newcastle-on-Tyne. The Examiners in Chemistry were Dr. Bernard Dyer, D.Sc. (Lond.), F.I.C., and Dr. W. Palmer Wynne, D.Sc. (Lond.), F.R.S., F.I.C. The Examiner in Therapeutics, Pharmacology, and Microscopy was Dr. Thomas Stevenson, M.D. (Lond.), F.R.C.P., V.-P.I.C.—(*For the Fellowship, F.I.C.).

A New Method for the Preparation of Non-saturated Hydrocarbides.—L. Tschugaeff.—This new method rests on a splitting-up undergone by certain xanthogenic derivatives when submitted to dry distillation. If, for example, we distil the xanthogenic ethers of the general formula $C_nH_{2m-1}O.CS.SR$, where R represents an alcoholic radicle, a decomposition takes place according to the following equations:—



In both cases a non-saturated hydrocarbon is formed which it is easy to rid of the accessory sulphur products by distillation over metallic sodium. The transformation takes place at a relatively low temperature, and the returns are fairly satisfactory. We can in the same manner utilise the dixanthogenic compounds, which decompose according to the following equation:—



But in this case the formation of saturated hydrocarbides is much less satisfactory than it was previously. To transform menthol into menthane we add 16 grms. of sodium, in small quantities at a time, to a boiling solution of 100 grms. of menthol in 60–70 grms. of dry toluene, and heat for twenty hours on a sand-bath. After having separated the excess of liquid sodium we add the necessary quantity of CS_2 , and then treat the cooled solution with ICH_3 . In this manner we obtain methylic ether and methylxanthogenic acid, which crystallises in beautiful needles, fusible at 39° . When submitted to dry distillation, this compound decomposes, giving menthane and methylmercaptan as principal products. The boiling-point of the menthane is $167-168^\circ$; D_4^{20} : 0.8131, 0.8128,

0.8136. As for its rotatory power, the author found by two observations: $[\alpha]_D = +114.77^\circ$ and $+116.08^\circ$; that is to say, figures which are much more constant and much higher than those which have been given in chemical bibliography up to the present.—*Berichte*, vol. xxxii., p. 3332.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Asbestos.—Can any of your readers tell me where I can find a good account of asbestos and its physical structure? The works I am acquainted with give too meagre an account to be of any use.—GEOFFREY MARTIN.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2124.

ON ELECTRIC TOUCH AND THE MOLECULAR CHANGES PRODUCED IN MATTER BY ELECTRIC WAVES.*

By JAGADIS CHUNDER BOSE, M.A., D.Sc.,
Professor of Physical Science, Presidency College, Calcutta
(Continued from p. 51).

[Electrical Reversal in the Radiation Product.]

In the hypotheses given above, it was said that the reaction of the radiation product, or B variety, should be opposite to that of the substance in the normal condition, or in the A state. Thus a negative substance which by the action of radiation shows an increase of resistance during conversion from the A to the B state should exhibit a diminution of resistance when B variety is acted on by electric waves. The contrary would be the case with positive substances.

The following tabulated statement indicates the phenomena exhibited by two classes of substances:—

Sign of electric touch.	Action of radiation on the fresh or A variety of the substance.	Further action of radiation on the radiation product or B variety.
Positive, e.g., iron ..	Diminution of resistance.	Increase of resistance.
Negative, e.g., arsenic	Increase of resistance.	Diminution of resistance.

We have thus two distinct classes of phenomena dependent on the sign of electric touch. If K_A represents the conductivity of the fresh substance, and K_B the conductivity of the radiation product, then—

(1). With positive substances, as the conductivity of the radiation product is greater ($K_B > K_A$), the first action of radiation would be to produce a diminution of resistance. This diminution will continue to be exhibited till the maximum amount of B variety is produced. The further action of radiation now will be to re-convert B into A; but as $K_A < K_B$ there would now be produced a diminution of conductivity, and a galvanometer in circuit will indicate an electrical reversal. The re-converted A variety may again be transformed to a greater or less extent to B, and in this way a series of reversals may take place, due to the continued action of radiation producing oscillation in molecular or atomic groupings. I shall designate this as the phenomenon of radio-molecular oscillation.

(2). With negative substances the conductivity of the radiation product is less ($K_B < K_A$), and the first action of radiation will therefore be an increase of resistance. The phenomena exhibited by these negative substances will precisely be opposite to those shown by the positive substances.

The above is but an approximate representation of the phenomena. To be more accurate, one has to take into account the partial changes and the effect of radiation on these changed products. Thus, at first suppose the substance to be entirely made up of A variety (this would rarely be the case). The first flash of radiation converts a large portion of A into B, the substance now being a mixture of A and B. The action of the next flash would be to convert the unchanged A into B, and re-convert to a more or less extent B into A. The electric response will thus be very strong at the beginning, but will become continuously less and less. When the proportion of B into has attained a maximum value, the re-conversion of B into

A will become relatively large, and thus give rise to reversal effect.

I spoke of the conversion "to a greater or less extent" of one variety into the other. There is also the question of the relative stability of the two varieties under the given conditions. From the above it will be seen what possibilities there are in the way of different combinations, and the varied phenomena thereby rendered possible. I will presently describe some of the typical cases.

In the above it has been assumed that the reaction of B variety is opposite to that of A. As previously mentioned, in working with a silver receiver I found it, when fresh, exhibiting at first a diminution and, subsequently, an increase of resistance. The anomalous action may be explained by supposing the normal fresh silver Ag to be positive, and the radiation product Ag' negative. These two varieties would thus give rise to opposite reactions. To justify the assumptions made above, it became necessary to obtain by some other means a variety of silver Ag', analogous to the hypothetical negative variety].

Two Varieties of Silver.

After many unsuccessful attempts, I at last obtained a variety of silver which gives a moderately negative reaction (increase of resistance). Silver chloride was first precipitated by the addition of dilute hydrochloric acid to silver nitrate solution. The precipitate was then reduced to metallic silver by zinc filings, the excess of zinc being dissolved off by the action of HCl. This form of silver gives a negative reaction. Direct precipitation of silver produced by dipping a piece of zinc in AgNO_3 solution gives a positive variety. The negative product Ag' is perhaps better formed at relatively low temperatures, for the products obtained on certain warm days, the thermometer registering 27°C ., were very feebly negative, and passed into the positive state after an interval of twenty-four hours. But on cold days (temperature $= 22^\circ \text{C}$.) the products obtained were stable. I have specimens which have kept the negative property unimpaired for nearly three months. The negative property is not due to any accidental impurity, for pure silver obtained by Stas' method also gave the negative reaction. The negative reaction may, however, be supposed to be due to a thin film of chloride formed during reduction. I washed the Ag' with NH_3 , then with water, and, after drying, the result was still a negative reaction. I then carried out a parallel set of experiments with ordinary silver filings. Two separate quantities were taken; one was shaken with only HCl, the other was mixed with zinc filings, and the excess of zinc was dissolved off with HCl; the two specimens were then washed and dried. Both gave the positive reaction of ordinary silver. The above experiments are interesting for the production, by chemical means, of an allotropic variety analogous to the transitory radiation product.

There are other differences of electric behaviour between Ag and Ag'; for instance, when made into a voltaic cell, the two varieties give a P.D. of about 0.12 volt. There are other interesting peculiarities about this cell, the consideration of which is postponed to a future occasion.

Electric Reversal.

It now remains to be proved that the "radiation product" exhibits a change of sign of electric touch. The sensitiveness of certain substances belonging to each of these two classes is very great. On the other hand, in the transition from one class to the other, substances are met with the sensitiveness of which is rather feeble. The experimental verification of the hypotheses mentioned above seemed at first very difficult, as the reversed action was likely to be masked by the stronger normal action of the still unconverted portion of the substance. It however occurred to me that if slightly sensitive substances were taken, then the direct and reversed actions were likely to be obtained with less difficulty. For this reason I took for my first experiments arsenic, which is moderately

* A Paper read before the Royal Society, February 8, 1900.

adopted to this end varies with individual cases. In the case of arsenic, for example, the action of radiation is often to produce a very great increase of resistance, and thus convert the substance into a non-conductor. The pressure has therefore to be so adjusted at the beginning, that the substance can never become altogether non-conducting; the receiver is thus absolutely free from all effects, except those which are to be observed—viz., the effects due to continuous action of radiation. The time of exposure is accurately measured by counting the individual flashes of radiation due to interruption of the primary current in the Ruhmkorff coil by a tapping key. The conductivity of the substance at a given moment is inferred from the deflection of the galvanometer in circuit with the receiver. When feeble radiation is used, it takes an inconveniently long time to obtain reversals; there is, besides, a tendency of self-recovery in the receiver. In order to expedite the reversals, the incident electric radiation is made very strong.

Before entering into the detail of the results obtained, I will say a few words about the principal types likely to be met with. We may have the following:—

I. Substances in which the B state is unstable under the given conditions; the B state will therefore only persist during the action of radiation, the substance relapsing into the original condition on the cessation of radiation. Two cases are possible (i.) when the substance is positive, (ii.) when the substance is negative.

The latter case is exemplified by potassium. In the curve (Fig. 2), A and B represent the two molecular states. The substance being negative, A is more conducting; *a* represents the conductivity of the fresh specimen; the thick dots S S' . . . the individual flashes. It is seen that the effect of radiation is to produce a sudden diminution of conductivity, due to the transient formation of B variety with its diminished conductivity. The substance, electrically speaking, is highly elastic, and the limit of its elasticity is also very great. With the majority of substances, however, self-recovery is only possible when the narrow limit of elasticity is not exceeded.

II. In this class the radiation product is somewhat stable; the successive conversions from A to B and from B back to A are supposed to be complete. Probably there is no substance which exhibits this action in a perfect manner, but we have an approximation to this condition in the case of magnesium, which under proper adjustments shows successive complete reversals for a long time. The substance, however, after a time exhibits the effect of fatigue.

The curve given in Fig. 3 clearly exhibits the reversals. This curve also explains the behaviour of magnesium noticed in my last paper, which appeared very curious at the time. "It is sometimes possible to so adjust matters that one flash of radiation produces a diminution of resistance, and the very next flash an increase of resistance. Thus a series of flashes may be made to produce alternate throws of the galvanometer needle" ("On a Self-recovering Coherer," &c., *Proc. Roy. Soc.*, vol. lxx., p. 169).

The receiver was so adjusted as to give a deflection of five divisions.

The first flash of radiation produced an increased deflection of 50 divisions (magnesium having a positive electric touch); the second flash produced a further deflection of five divisions, the third flash produced a negative deflection of five divisions, the fourth flash produced + 5, the fifth flash gave - 50 divisions, and the sixth flash a deflection of + 50. The reversals followed each other almost regularly, till the substance became insensitive.

III. Lastly, we may have a class of substances where the conversion from one state to the other is not complete. Here, again, we get two sub-divisions, owing to the distinction between positive and negative substances.

Taking first the case of a positive substance (see Fig. 4, *B*), the original conductivity of which is represented by *a*, the action of the first few flashes of radiation would be to produce a great increase of conductivity by the

formation of B variety; the next flashes convert B back to A, but not completely, and the negative deflection will be less than the previous positive deflection. Owing to this "damping" effect, the oscillation curve will approximate to a logarithmic decrement curve. After a series of

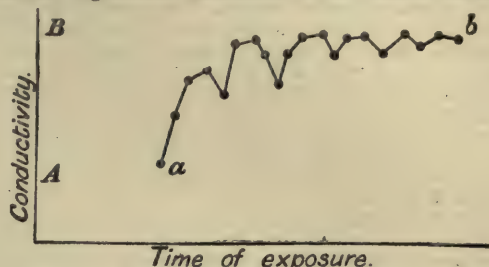


FIG. 5.—"DAMPED" OSCILLATION CURVE FOR A POSITIVE SUBSTANCE.

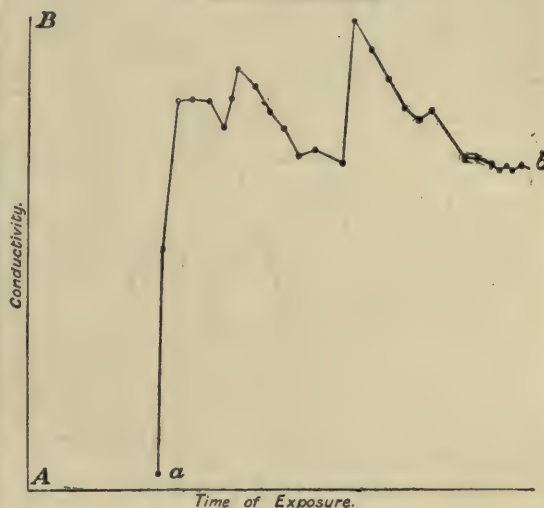


FIG. 6.—CURVE FOR IRON.

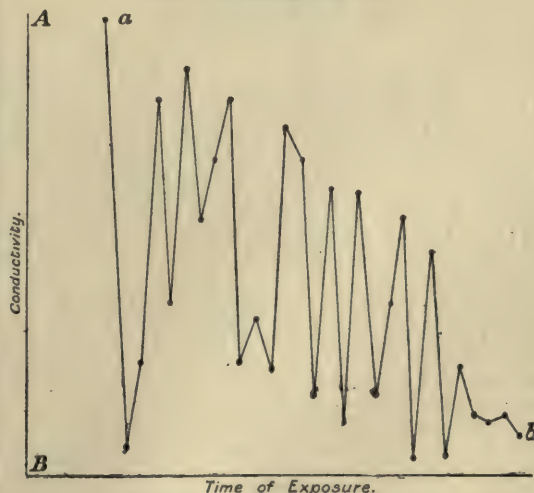


FIG. 7.—CURVE FOR ARSENIC.

reversals the oscillation dies away, and the substance becomes almost inert. A glance at the hypothetical curve to the right shows that at the inert stage, *b*, the substance as a whole ought to become more conducting than the fresh specimen, *a*.

The opposite should be the case with negative substances (see Fig. 4, a).

Fig. 5 exhibits the actual curve obtained with a compound positive substance.

It is remarkable for its regularity. The next figure (Fig. 6) gives the curve for iron. The first diminution of resistance is too great to be properly represented in the diagram. Here we have the same type as in the previous case; *the inert stage, b, is also more conducting than a.*

IV. I will now consider the case of a negative substance exhibiting damping; arsenic will be taken as an example where the damping is not so great as in the case of iron.

Fig. 7 represents the actual curve obtained with arsenic (compare with the hypothetical curve for a negative substance, Fig. 4, a).

It will be observed that *the substance in the fatigued state is, on the whole, less conducting than in the fresh condition*, as we are led to expect from the hypothetical curve. It will also be seen that the oscillations are very regular towards the end. The curves given in Figs. 6 and 7 are those obtained with specimens immediately after they were set up. Had I allowed them a period of rest to allow the particles to get properly settled, I would have got curves even more regular. It is, however, evident that in substances exhibiting damping, two opposite electric conditions are induced in fatigued specimens; the positive becomes on the whole more conducting and the negative less conducting than in the fresh specimens. At the inert stage the rate of mutual conversion from one state to the other probably becomes equal, and the apparent fatigue is thus not due to the absolute want of sensitiveness of the constituent varieties, but to the opposite reactions of A and B balancing each other.

We may now apply some further crucial tests to verify the suppositions made above.

(To be continued).

ON THE COMPOSITION OF N. S. WALES LABRADORITE AND TOPAZES, WITH A COMPARISON OF METHODS FOR THE ESTIMATION OF FLUORINE.*

By G. HARKER, B.Sc.

(Concluded from p. 57).

Results obtained by the Tetrafluoride Method on Calcium Fluoride, Cryolite, and Apatite.—First Series.—The substance was fused with sodium potassium carbonate and then decomposed. The calcium fluoride used in these experiments was from ground crystals, and on testing, by conversion into calcium sulphate, gave 99.6 per cent of calcium fluoride. Four experiments gave 44.60, 45.97, 46.12, and 46.20 per cent, the theoretical percentage of fluorine being 48.53 and the average difference 2.82 per cent.

Second Series.—The substance was decomposed without previous fusion with alkaline carbonates. The calcium fluoride in the first four of these experiments was from crystals of fluor-spar ground, and evaporated to dryness with hydrofluoric acid to get rid of silica, and then ignited. On testing by conversion into calcium sulphate they gave 99.8 per cent of calcium fluoride.

	Amount taken. Grms.	Percentage of fluorine found.
1	0.1565	45.90
2	0.2722	47.08
3	0.5212	47.21
4	0.2900	46.64
5	0.1736	46.31
6	0.1787	45.95

The theoretical percentage was 48.62 and the average difference 2.25 per cent. These results were corrected for the solubility of potassium silicon fluoride, which was found to be 0.0016 gm. in 50 c.c. of a 50 per cent alcohol solution. Nos. 5 and 6 were precipitates of calcium fluoride obtained by Berzelius's method from the Mudgee topaz.

Cryolite similarly gave 52.17 per cent when previously fused with alkaline carbonates, and 52.62 without previous fusion, and when treated by Berzelius's method 55.34. Apatite gave 2.80 by the first method and 2.81 by the second.

Application of the Tetrafluoride Method to Topaz.—The Mudgee topaz by this method gave only 13 per cent of fluorine, which was much too low. When repeated on the Brazilian topaz a similar low result was obtained, viz., 10.9 per cent. It seems, therefore, that this method works well for minerals not containing silica. That it is the presence of silica in the topaz which causes the error was shown by adding silica to calcium fluoride or topaz before fusing, when in all cases a much lower result was obtained, the error being larger as more silica was added. Thus calcium fluoride gave 36.54 and 35.06 per cent of fluorine, and topaz 7.05 and 4.26 per cent, results much lower than those obtained when silica was not added.

Third Method, Fusion with Alkaline Carbonates and Silica.—A third method for the determination of fluorine was then tried, viz., that of Berzelius as modified by Rose. The ground topaz is fused with one-half its weight of pure silica; the fused mass extracted with water; 5 to 10 grms. of ammonium carbonate added to precipitate silica, and the solution allowed to stand twelve hours. The solution is filtered and evaporated to get rid of excess of ammonia, and a solution of zinc carbonate in ammonia added to precipitate any silica in solution. The liquid is then further evaporated to get rid of ammonia, filtered from zinc oxide and silicate, and the fluorine precipitated by calcium chloride in the usual manner.

The results from the Mudgee topaz were much higher than those obtained by the two previous methods, and were constant; the same constant results were obtained in the case of the Brazilian topaz and the green topaz from New England.

The calcium fluoride obtained by precipitation in this method from the Mudgee topaz was tested and found to be free from calcium silicate. Berzelius's method therefore gave the best results for fluorine in topaz; but as there seemed to be no reason why the fluorine should be lost in Wöhler's method, which did not apply equally to that of Berzelius's, an attempt was made to find where the fluorine was lost in the former case.

It was found that no fluorine is left in the residue after extracting the fused mass with water. The decomposition in Wöhler's method is therefore complete. It was noticed that the precipitate of aluminium hydroxide obtained on addition of ammonium carbonate to the solution was more granular than the usual gelatinous precipitate, and on trial this precipitate was found to contain no silica, but always more or less fluorine. (Hydrofluoric acid was liberated from the precipitate by sulphuric acid and etched glass. Mixed with silica and sulphuric acid, silicon tetrafluoride was given off, which was passed into water and the potassium silicon fluoride precipitated). On one occasion 6.6 per cent of fluorine was obtained in this precipitate by Berzelius's method, but this was exceptionally large, the usual amount not being more than 1 to 3 per cent. When the ammonium carbonate was added hot to the solution, and then allowed to stand until quite cold, a larger proportion of fluorine was found in the precipitate than when it was filtered hot, the precipitate containing the fluorine coming down on cooling. This precipitate contained a larger amount of fluorine when sodium potassium carbonate was used than when sodium carbonate alone was employed. In obtaining the results given by Wöhler's method for fluorine, sodium potassium carbonate was frequently employed, which accounts for

* Read before the Royal Society of N. S. Wales, December 6, 1899.

some of them being so low, but, even when sodium carbonate alone was employed, the highest percentage obtained was 12.69.

On adding the amount of fluorine recovered from the precipitate to the amount obtained from the solution after the addition of ammonium carbonate, the total is nearly the same as that obtained by Berzelius's method. Thus 14.2 per cent was obtained from Brazilian topaz by Berzelius's method. In one experiment 6.92 per cent was obtained from the solution and 6.50 from the precipitate, total 13.42 per cent. In a second experiment 12.69 from the solution and 1.21 from the precipitate, total 13.90 per cent. This seems to show that Berzelius's method gives the total fluorine present. The precipitates of calcium fluoride were tested by conversion into calcium sulphate. The residue obtained on treating the fused mass with water in Wöhler's method contained all the silica and about two-thirds of the alumina and some soda, and had approximately the constitution $3\text{SiO}_2, 2\text{Na}_2\text{O}, 2\text{Al}_2\text{O}_3$. On boiling with water the soda and alumina were slowly removed, but to what extent this could be carried out was not determined. In the case of Berzelius's method the residue contained all the aluminium. The silica prevents the aluminium from passing into solution, and thus stops the loss of fluorine which occurs in Wöhler's method. The amount of silica necessary to do this was found to be 31.6 per cent in the case of the Brazilian topaz.

Examination of the Ammonium Carbonate Precipitate.—The topaz was fused with sodium carbonate alone and the fused mass dissolved in water and filtered. Ammonium carbonate was added to the hot solution, and a gelatinous precipitate, consisting chiefly of aluminium hydroxide, formed. After filtering and cooling a more granular but still gelatinous precipitate separated out and collected at the bottom of the beaker. This was filtered off and examined. Only a small amount was obtained, which on drying became powdery and fused at a red heat. The sodium and aluminium were determined by conversion into sulphates, the fluorine by fusion with silica and alkaline carbonates. 0.0210 gm. heated to redness gave 23.8 per cent sodium, 26.2 per cent aluminium; and 0.200 gm. gave 33.3 per cent of fluorine, leaving oxygen by difference 16.7 per cent. Assuming some of the aluminium to be combined with the oxygen as alumina due to imperfect separation of the fluorine precipitate from aluminium hydroxide, we have for the composition of the former fluorine, precipitate sodium 36.8, aluminium 11.7, and fluorine 51.5 per cent. Cryolite requires 32.9, 12.8, and 54.3 per cent.

In another experiment on a different precipitate 0.0130 gm. gave sodium 20.8, aluminium 29.2 per cent, and 0.201 gm. gave 30.8 per cent of fluorine, hence oxygen by difference 19.2 per cent. Allowing for alumina this gives sodium 35.1, aluminium 13.0, fluorine 51.9 per cent.

It seems probable therefore that the fluorine is precipitated as a double fluoride of sodium and aluminium. Like cryolite, this precipitate also fuses readily. But as the amounts analysed were so small, it is proposed to confirm the results by working with larger quantities.

Comparison of the various Methods for Fluorine on the Topazes.

	1. Fusion with alkaline carbonates.	2. Tetra- fluoride.	3. Fusion with alkaline carbonates and silica.
N. S. W. topaz from Mudgee	5, 11.01	12.93	17.04, 17.60, 17.10
Brazil	4.73, 11.2, 11.71, 11.21, 6.92, 12.69	10.90	14.23, 14.61
New England topaz	—	—	16.30, 15.92

A table is given above showing the results obtained by the various methods for fluorine, on the topazes. While obtaining the percentages for fluorine by methods (1) and (3), the silica and alumina were also estimated, so

that, with the exception of water, the whole of the constituents were now obtained.

It has been found by Penfield and Minor (*Am. J. Sci.*, 94) and Jannasch and Locke (*J. Chem. Soc.*, 94) that all topazes contain more or less water of constitution. The former found 2.45 and the latter 2.69 per cent in Brazilian topaz. The water takes the place of the fluorine. Penfield and Minor decomposed the topaz with sodium carbonate, and the water free from acid was weighed in sulphuric acid or calcium chloride tubes. Jannasch and Locke decomposed with litharge in a bulb tube and collected the water in a calcium chloride tube, a stream of dry air being passed through the apparatus. This last method was found more convenient, as a much lower temperature could be used to decompose the topaz; both methods, however, gave the same results. In the experiments the topaz was first heated to bright redness over a strong Bunsen to drive out any contained water; it was then decomposed by litharge and its so-called water of constitution determined. Blank tests on the litharge showed that the calcium chloride tube gained 2 to 3 decim. grms., and in calculating the percentages this was deducted. In the experiments about 0.5 gm. of topaz was mixed with 2 to 2.5 grms. of previously heated litharge, the same amount of litharge being used in the blank tests.

Water of Constitution.

Locality.	Amount taken. Grm.	Water found.	Percentage.
Brazil	0.6324 0.5080	0.0134 0.0107	2.12 2.11
New England	0.5038 0.5780	0.0050 0.0066	0.99 1.14
Mudgee	0.4900 0.4958	0.0038 0.0038	0.78 0.73

Results of Analysis.—Appended is a table giving the complete analyses of these three varieties of topaz. In the latter it will be seen that the silica and alumina obtained by Wöhler's method are always higher than by Berzelius's, and this is apparently due to the aluminium hydroxide taking down with it some of the fluorine and sodium.

The alumina was always tested by potassium bisulphate, and the silica by hydrofluoric acid purified from the commercial acid by re-distilling in a platinum retort. The calcium fluoride precipitates were tested by conversion into calcium sulphate or in some other way.

Analysis of Topazes.

	Fusion with alkaline carbonates and silica.	Fusion with alkaline carbonates alone.			
	1.	2.	1.	2.	
Mudgee, N. S. W.					
SiO ₂	31.90	31.84	32.30	32.46	
Al ₂ O ₃	56.62	56.80	59.70	59.21	
F	17.60	17.00			
H ₂ O on ignition	0.23	0.26			
H ₂ O by PbO ..	0.75	0.75			
	107.10	106.65			
Brazil.					
SiO ₂	31.95	32.16	32.31	31.90	32.18
Al ₂ O ₃	54.52	54.61	55.90	56.45	55.88
F	14.62	14.23			
H ₂ O on ignition	0.23	0.30	0.26	0.24	0.26
H ₂ O by PbO ..	2.12	2.12			
Fe ₂ O ₃	—	—	—	0.10	0.09
	103.44	103.42			
New England, N. S. W.					
SiO ₂	31.73	31.92			
Al ₂ O ₃	55.62	55.43			
F	16.30	15.92			
H ₂ O on ignition	0.37	0.39			
H ₂ O by PbO ..	1.07	1.07			
Fe ₂ O ₃	0.12	—			
	105.21	104.73			

the supernatant fluid is perfectly clear and transparent. To arrive exactly at this condition it is preferable to stop the addition of the sodic carbonate when the solution has only a slight yellow tint, as a little extra stirring invariably causes this to disappear. At this stage the solution, which possesses a distinct acid reaction, but is nevertheless free from iron or alumina, is transferred to a half-litre flask and diluted to the mark; then, after a thorough mixing by shaking, filtered through a ribbed filter: 400 c.c. of the clear filtrate are now exactly measured off into a flask of about 600 c.c. capacity, 20 c.c. of a saturated solution of sodic acetate and 10 c.c. of acetic acid added, and the whole then raised nearly to the boiling-point. A current of sulphuretted hydrogen is then passed through the solution, allowing the gas to pass until the contents of the flask are nearly cold; the sulphides of cobalt, nickel, and zinc will then be found to have been completely precipitated free from impurities, and may now be filtered off, washed with water containing sulphuretted hydrogen, then dried and ignited. The ignited oxides and any sulphide which may remain attached to the sides of the flask are now dissolved in strong hydrochloric acid with the aid of a drop or two of nitric acid, and evaporated twice to dryness with hydrochloric acid, so as to completely get rid of all nitric acid, the residual chlorides dissolved in from 5 to 10 c.c. water, and allowed to become cold. The solution of the metals thus obtained may through careless neutralisation contain a little iron, so that for greater security it is always better to add a slight excess of an emulsion of oxide of zinc, and filter off any trace of ferric oxide which may be thrown down.

The filtrate, which is now entirely free from iron, is diluted to about 50 c.c., and well mixed with from 10 to 15 c.c. of a 10 per cent solution of hydrogen peroxide, and then with 10 c.c. of a 10 per cent solution of potassic or sodic hydrate; the cobalt is immediately precipitated as sesquioxide, Co_2O_3 , whilst the nickel is simply thrown down as the green hydrated monoxide. The mixed precipitate is now boiled for about a minute, so as to ensure the complete decomposition of the excess of hydrogen peroxide, allowed to cool, and then transferred to a stoppered bottle and digested with an excess of potassic iodide and hydrochloric acid until the decomposition is complete; then the iodine thus set free titrated in the usual manner with sodic hyposulphite, $1 \times 0.46511 = \text{Co}$. The potassic or sodic hydrate employed in this process must be previously examined for impurities which can liberate iodine from potassic iodide; samples containing nitrites, for example, are not uncommon.

As illustrating the accuracy of this process, the following examples will show what may be expected:—

Two lots of ore, each of 2½ grms., were treated as described, A without any addition; whilst to B, 10 c.c. of a perfectly pure solution of cobalt, containing 0.0920 gm. of CoO , were added immediately after the mineral was dissolved.

	A.	B.	Difference.	ERROR.
1.	4.21	7.91	3.70	0.02 % CoO
2.	6.67	10.38	3.71	0.03 "
3.	6.84	10.53	3.69	0.01 "
4.	7.73	11.43	3.70	0.02 "

Essence of Chrysanthemum.—G. Perrie.—Essence of chrysanthemum is a greenish liquid of an oily consistency, with a special odour recalling both that of peppermint and camomile; it begins to boil at 150° , its density is 0.932 at 15° , and its index of refraction at 18° is 1.4931. It is soluble in ten parts of alcohol at 95° , but almost insoluble in alcohol at 70° . When cooled down to -15° it deposits a small quantity of an amorphous solid product, probably a paraffin; at -24° it becomes very thick, and solidifies completely in a mixture of ether and solid carbonic acid.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 6.

THE ANALYSIS OF CHROME AND TUNGSTEN STEELS.

By A. G. M'KENNA.

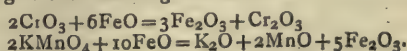
THE writer has had occasion during the past few years to make complete analyses on several hundred samples of steel, containing both chromium and tungsten, and has found the following methods very satisfactory, accurate results being obtained without excessive care or unusual precautions.

The steel is usually too hard to be drilled, and is broken up in a steel mortar until no single piece is larger than a grain of rice. For the determination of sulphur, silicon, tungsten, manganese, and chrome, 5 grains are weighed into a 500 c.c. evolution flask, so arranged that the gases evolved on the addition of 30 c.c. hot water and 30 c.c. concentrated hydrochloric acid shall be absorbed by an ammoniacal cadmium chloride solution contained in a large test-tube. The solution is made as rapidly as possible by the application of heat, as there seems to be evidence that with some irons lower results are obtained by the evolution method when cold acid is used. When the steel has dissolved the solution is boiled for a minute or two until no more hydrogen remains in the flask, being displaced by steam. The sulphur is then determined by titration with iodine in the usual manner, using starch solution as an indicator. By adding a few grains of zinc chloride to the starch solution it can be kept indefinitely without spoiling. The solution in the evolution flask is transferred to a 500 c.c. Erlenmeyer flask, 10 c.c. of strong HNO_3 added, and evaporated to dryness on a hot plate, taken up with 15 c.c. strong HCl , evaporated again to dryness, taken up in 20 c.c. strong HCl , diluted with hot water to about 100 c.c., boiled, and filtered. All the silica and tungstic acid will be on the filter-paper; after washing thoroughly with a 5 per cent HNO_3 solution, the residue is ignited in a weighed platinum crucible, $\text{WO}_3 + \text{SiO}_2$, and weighed. A few drops of HFl are now added, and the crucible is heated to a bright red for five minutes to volatilise silica. The loss is silica, which is calculated to silicon; the residue in the crucible is tungstic acid, which is calculated to tungsten. This residue generally contains a trace of iron oxide, which can be easily determined by fusing the residue, after weight has been taken, with sodium carbonate, and filtering off the oxide of iron after solution in hot water.

The filtrate from the tungstic acid and silica is again transferred to an Erlenmeyer flask and evaporated to low bulk; 50 c.c. of concentrated HNO_3 are now added, and the solution boiled until no more fumes come off, showing that all hydrochloric acid has been removed. Enough concentrated HNO_3 is added to make the volume 200 c.c., and the solution again heated. When it has reached the boiling-point, 10 grains of potassium chlorate are added, and the solution boiled down to 75 c.c. in order to remove all chlorine.

The manganese will now be completely precipitated as MnO_2 , and the chromium will be converted to chromic acid.

The solution is filtered on an asbestos plug while hot, and washed a few times with freshly boiled concentrated nitric acid. In the filtrate chromium is determined by titration with ferrous sulphate and permanganate according to the following reactions:—



If the solution is diluted to about 500 c.c., and cooled to about 20°C . before titration, there is not the slightest danger of interference by the nitric acid. The MnO_2 on the asbestos plug is dissolved by hot hydrochloric acid and a pinch of potassium nitrite. It is brought to a boil to drive off chlorine and the traces of iron precipitated by ammonia and ammonium acetate; the basic precipitate is dissolved and re-precipitated to free from traces of

manganese. In the filtrate manganese is precipitated by bromine in a strongly ammoniacal solution, filtered, ignited, and weighed as Mn_2O_3 .

For the determination of phosphorus 5 grms. is weighed into a porcelain dish, and 60 c.c. of dilute nitric acid added. If the steel contains more than 1 per cent of chromium, it will probably be found necessary to add HCl from time to time to secure solution. Solution must be complete before allowing the evaporation to go too far, or it will be found almost impossible to dissolve the last particles of steel.

The solution is baked as usual in phosphorus determinations, 20 c.c. HCl added and again taken to dryness, taken up in 20 c.c. HCl again, diluted and filtered from tungsten and silicon, which may be ignited and weighed as a check on the first determination. To the hydrochloric acid solution 35 c.c. strong ammonia is added, then sufficient strong nitric to re-dissolve the hydrate of iron: 100 c.c. molybdate solution, made according to Wood's formula as given by Blair, is added to the flask, which is then shaken for a few minutes to ensure complete precipitation of the phosphorus. After standing for an hour the yellow precipitate is filtered on a dried weighed paper, washed with dilute 1 per cent nitric acid, dried for an hour, and weighed as phospho-molybdate, containing 1.63 per cent phosphorus.

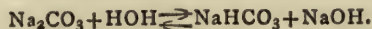
For carbon, 1.5 grms. are dissolved in 100 c.c. of a 33 per cent copper and potassium chloride solution. After standing half an hour 5 c.c. HCl is added to hasten solution. When all the precipitated copper has re-dissolved, the solution is filtered through ignited asbestos in a platinum filter tube, using suction to hasten filtration. The carbon on the plug is washed a few times with hot water, then dried and burnt in a platinum tube with a stream of oxygen. The CO_2 is absorbed as $BaCO_3$ in a barium hydrate solution contained in a ten-bulb absorption tube, filtered, washed well with freshly boiled distilled water, ignited, and weighed as $BaCO_3$ containing 6.09 per cent carbon.—*Proceedings of Engineers' Society of Western Pennsylvania*, xvi., No. 4.

ESTIMATION OF ALKALI CARBONATES IN THE PRESENCE OF BICARBONATES.*

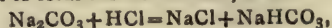
By FRANK K. CAMERON.

Introduction.

In an aqueous solution sodium carbonate is hydrolysed to a definite extent, depending upon the concentration and temperature conditions. This may be represented thus:—



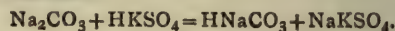
Of the four electrolytes then present in the solution only the sodium hydroxide is dissociated or ionised to any considerable extent, and in consequence the solution presents the characteristic features of a solution of this substance—it is markedly alkaline. Shields (*Ztschr. Phys. Chem.*, 1893, xii., 167), has found the amount of this hydrolysis for a tenth-normal ($N/10$) solution of sodium carbonate at 25° C. to be about 3.17 per cent. For certain purposes it is desirable to determine the "alkalinity" of such a solution, that is to say, the amount of sodium ions which may possibly result from this hydrolytic action, or one-half the sodium which has been brought into the solution as sodium carbonate. This may be done by titrating the solution with a standard acid solution. But this procedure usually requires that the solution should be heated to the boiling temperature. At the ordinary temperatures the acid reacts with the sodium carbonate to some extent to form the bicarbonate, thus:—



* Contribution from the Division of Chemistry, U.S. Department of Agriculture. From the *American Chemical Journal*, vol. xxiii., No. 6.

and this formation of the bicarbonate may possibly be augmented by some of the liberated carbonic acid acting on the still undecomposed carbonate. Acid sodium carbonate is itself neutral towards indicators, and in consequence totally misleading results are inevitable. Furthermore, the presence of bicarbonates in the solution, other than that formed by the hydrolytic action of the water, will render an estimation of the sodium alone utterly valueless. The problem has been presented in this laboratory to estimate the amount of sodium carbonate in mixtures containing also the bicarbonate, and, further, to do this without heating the material. Many attempts have been made by others to devise a method for this purpose. That proposed by Winkler has probably proved the most satisfactory. A good description of it has been given by Küster (*Ztschr. Anorg. Chem.*, 1896, xiii., 127). But this method was not adapted to our purposes for several reasons. The method of Sundstrom described by Lunge (*Ztschr. Angew. Chem.*, 1897, 41), as well as that devised by Lunge (*Ztschr. Angew. Chem.*, 1897, 169) himself, were also found to be impracticable under the conditions which confronted us. Without going into greater detail it may be said that no method of which a description could be found in the literature was free from serious objections. This appeared most surprising in view of the probable technical value of such a method in the manufacture of sodium carbonate. The problem has been satisfactorily solved, and an account of the preliminary work on it may be found elsewhere (*Report No. 64*, U.S. Department of Agriculture, Division of Soils). It was deemed advisable, however, to give the method a more critical examination. The results are recorded in this paper.

Acid potassium sulphate is a well-characterised strong acid. With sodium carbonate it has been shown to react as here indicated:—



The reaction-products, sodium bicarbonate and sodium potassium sulphate, are neutral towards the ordinary indicators. Therefore by titrating a solution containing sodium carbonate with a standard solution of sodium or potassium bisulphate, the amount of sodium carbonate present can be determined directly. Obviously the same statements may be made regarding potassium carbonate. Many indicators have been used with this method, but it may be said at once that, while good results can be obtained with others, phenolphthalein lends itself pre-eminently to the purposes here in view, and it alone is now used in this work in this laboratory. It is to be regretted that the reverse procedure from that just stated cannot be followed, for to the majority of analysts it would certainly be easier to titrate to the appearance of colour rather than to its disappearance. But in this case such a procedure is entirely inadmissible because the sodium carbonate, on being brought in contact with an excess of the strong acid, is more or less decomposed, with the evolution of carbon dioxide, and misleading results that are not comparable are obtained.

It has become evident, in the course of the investigation, that acid sodium carbonate is a very unstable salt, especially in water solutions. The sodium carbonate solutions which had been titrated to loss of colour, immediately began to colour again on standing, the rate of this "inversion" being a function of the concentration and the temperature, as well as time. Some solutions which had been titrated just to loss of colour at 1° C., had practically no colour at the end of an hour, but on being gradually warmed over a Bunsen flame very soon became strongly coloured from the reaction of the regenerated sodium carbonate on the phenolphthalein present. A tenth-normal solution, titrated just to loss of colour, at the room temperature (about 25° C.) will show a marked pink colour within five minutes, and a strong colour within half-an-hour.

A solution of sodium carbonate was divided into a

number of portions in small Erlenmeyer flasks, and coloured by the addition of phenolphthalein or litmus. Carbon dioxide was passed in until the solutions no longer showed any alkaline reaction with the indicators. They were then allowed to stand for several days. Some of the flasks were closed with rubber stoppers. The open flasks very soon showed a strong alkaline reaction. In the closed flasks, while a faint alkaline colour appeared within a very short time, the colour became more intense, but very slowly, showing the influence of the carbon dioxide in retarding the inversion. Nevertheless, it would appear that the inversion does take place, even though some carbonic acid must be present. This phase of the subject is now being studied in this laboratory, and the investigation will be continued as time and opportunity may permit.

In a qualitative sense precisely similar results were obtained with potassium carbonate and with sodium silicate, of which both yield acid salts which are unstable in water, and at once invert to a greater or less extent. Sodium borate and disodium phosphate, being salts of weak acids, give an alkaline reaction in water solutions, and can be very conveniently titrated to neutrality with acid potassium sulphate, but in neither case was any subsequent inversion observed.

Description of Experiments.

After some preliminary work it was deemed advisable to test the method by referring all solutions to a standard alkali solution, rather than by making the numerous gravimetric determinations which would otherwise be required. All the titrations were made from two burettes which previous experience had shown to be quite reliable. It was not thought necessary to calibrate them. The burettes were graduated to tenths (0.1 c.c.) and smaller readings could be estimated. It was thought preferable, however, not to attempt readings closer than one-half a scale division (0.05 c.c.), but to depend upon the average of a series of readings.

The standard for reference was a solution of potassium hydrate, accurately prepared and carefully freed from carbonates or other impurities. It was so prepared as to contain 18.17106 grms. of potassium hydroxide per litre. A solution of approximately tenth-normal acid potassium sulphate was then made up and compared with the standard potassium hydrate solution. It was found, as a result of a satisfactory series of titrations, that 1 c.c. of the potassium hydrate solution was equivalent to 6.764 c.c. of the acid potassium sulphate solution. It follows that 1 c.c. of the acid potassium sulphate solution contained 0.006518 gm. of the acid salt, whereas a tenth-normal solution (N/10) would contain 0.006758 gm.

Reasonably pure potassium bisulphate is not difficult to obtain. But one cannot always be certain that an otherwise satisfactory sample contains precisely those proportions of the elements involved, which are required by the formula HKSO_4 . A small excess of either sulphuric acid or the potassium sulphate will not materially alter the value of the reagent for the purposes under discussion, but it is obvious that for very accurate work it is safer to determine the concentration of the solution in the manner just described, rather than depend on either a gravimetric determination of the sulphuric acid alone or of the potassium it contains.

A solution of potassium carbonate (approximately tenth-normal) was then prepared and titrated with the results here given, the first column indicating quantity of potassium carbonate, the second column the quantity of potassium bisulphate, and the third column the ratio of the readings:—

TABLE I.

10.00	12.70	1.270
15.00	18.90	1.260
15.00	18.90	1.260
20.00	25.20	1.260
20.00	25.20	1.260
		1.262

These titrations were made in the usual manner by adding a little of the acid solution, shaking, and waiting a few moments to see if colour disappeared before proceeding.

The potassium carbonate was then analysed in the following way:—The solution was treated with an excess of hydrochloric acid, boiled to drive off all the carbon dioxide liberated, and the excess of acid determined by titration with the standard potassium hydrate solution. The figures follow. The first column represents amount of potassium carbonate, the second column hydrochloric acid, and the third column potassium hydrate:—

TABLE II.

40.00	20.00	7.15
40.00	20.00	7.15
40.00	20.00	7.20
		7.166

By a careful and satisfactory series of titrations 1 c.c. of the hydrochloric acid solution was shown to be equivalent to 1.0464 c.c. of the potassium hydroxide solution. Therefore:—

20 c.c. HCl solution = 20.928 c.c. KOH solution.
Excess " " = 7.166 " " "

40 c.c. Na_2CO_3 " = 13.762 " " "
1 " " " = 0.344 " " "

It has been shown that 1 c.c. KOH solution was equivalent to 6.764 c.c. HKSO_4 solution; therefore, 0.344 c.c. KOH solution was equivalent to 2.327 c.c. HKSO_4 solution. But since only one-half as much acid potassium sulphate is required to convert the potassium carbonate to bicarbonate, it should have required $2.327 \div 2$, or 1.163 c.c., instead of 1.262 c.c. as actually found. This disagreement was startling in view of the good results previously obtained with the method.

A sodium carbonate solution of about the same strength as the potassium carbonate solution just described was prepared and a long series of titrations made in the manner as with the potassium carbonate solution. It was found that 1 c.c. of the carbonate solution was equivalent to 1.137 c.c. of the acid sulphate solution, though an analysis made in the same manner as in the case of the potassium carbonate showed that 1.035 c.c. of the acid sulphate solution should have been required. The disagreement was practically the same in both cases.

(To be continued).

THE USE OF CARBIDE OF CALCIUM IN METALLURGY.

As is well known, carbide of calcium is principally used for the manufacture of acetylene gas; the steady increase of this means of lighting justifies the existence of the numerous installations which have been erected, especially in the Alps, with a view to the production of large quantities of this substance.

It is, however, a matter of some importance to this new industry that the substance in question should find some other applications, and with this end in view we think it advisable to point out the part it is able to play in metallurgy.

Carbide of calcium is a deoxidising agent; if therefore to a metal in the state of fusion, which is always slightly oxidised, carbide of calcium is added, either alone or with quicklime, the general reaction should be as follows:— $\text{CaC}_2 + 2\text{MO} = 2\text{CO} + \text{Ca} + 2\text{M}$.

It is evident that under these conditions, as one part only of the CaC_2 takes part in the reaction, the utilisation of this body would not be very great. To increase its

power, a metallic chloride, RCl , must be added, the chlorine of which will combine with the Ca set at liberty in such a manner that the two affinities of the C for the O, and of the Ca for the Cl, will act simultaneously:— $\text{RCl} + 2\text{MO} + \text{CaC}_2 = \text{R} + 2\text{M} + \text{CaCl} + 2\text{CO}_2$.

These reactions may be applied either to the extraction of a metal from its ores or for the manufacture of metallic alloys, according to whether the metallic chloride taken corresponds with the metal or not.

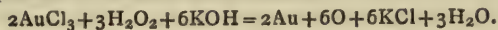
If $\text{M} = \text{R}$, we obtain the metal M only; if not, we obtain the alloy $\text{R} + 2\text{M}$. We may quote as an example of the last formula the preparation of aluminium bronze, which consists of gently heating a mixture of alumina and chloride of copper, in contact with carbide of calcium.—*Revue Générale des Sciences*, June 30, 1900.

RESEARCHES ON GOLD.

THE ESTIMATION OF GOLD, AND ITS SEPARATION FROM PLATINUM AND IRIDIUM.

By L. VANINO and L. SEEMANN.

THE method consists in treating the solution containing the metals with peroxide of hydrogen after the addition of an alkaline lye. While other methods require several hours to effect a complete reduction, in this case the gold is precipitated in a few minutes, even in the cold, as a black deposit which under the action of heat agglomerates and becomes of a reddish brown-colour:—



In the case of dilute solutions it is best to apply heat after the precipitation, then acidulate with HCl . For the estimation of gold in commercial chloraurate of sodium it is, however, preferable to effect the reduction by means of formic aldehyde instead of peroxide of hydrogen.

The reaction of peroxide of hydrogen in alkaline solution is much more sensitive qualitatively than any other reaction of gold. With 3 milligrams of gold per litre we can still perceive a pale reddish colouration, appearing blue by reflected light; this would not be detected by other reagents.

Silver is also precipitated quantitatively under the same conditions, but platinum as well as iridium remains in solution; this affords an excellent method for separating these two metals from gold.—*Berichte*, vol. xxxii., p. 1698.

NOTICES OF BOOKS.

Annual Report on the Year 1899. E. MERCK. Darmstadt. March, 1900. Pp. 177.

THE kindly reception which this publication has met with during the last ten years has necessitated a continuous increase in the edition, which has now reached a total of 30,000 copies.

Since the last report the author states he has produced a satisfactory tuberculosis toxin, both from bouillon and from the bacteria (*German patent*, 108,593), thereby nearing the solution of the antituberculosis question. The preparation of this toxin rests upon the fundamental view that both the poisons which pass into solution in the bouillon and those remaining in the bodies of the bacteria should jointly be employed as the initial material for the treatment of tuberculosis: a preparation of this kind has been introduced under the name of "tuberculol."

Another novelty introduced by Mr. Merck is an antidote apparatus for use in cases of poisoning by prussic acid and cyanide of potassium. One method of dealing with cyanic poisoning is by resorting to artificial respiration, evacuation of the stomach, the use of stimulants,

&c.; this, however, has proved successful in light cases only. A second method consists in the use of nitrate of cobalt: the injection of large doses of this salt may cause a diminution, or even disappearance, of the symptoms of cyanic poisoning, although the fact cannot be explained chemically. The third method is based on the conversion of the hydrocyanic acid into a haloid compound. The fourth method involves the principle of the conversion of prussic acid within the system into oxamide by means of peroxide of hydrogen, according to the formula $2\text{CNH} + \text{H}_2\text{O}_2 = \text{C}_2\text{O}_2\text{N}_2\text{H}_4$. This method is the most successful of the four mentioned, and the apparatus devised is for its special application.

There is also a full description of a large number of preparations, some of which have already been noticed in these columns under the heading of "Merck's Digest."

The book concludes with four excellent indices, viz., a general index, a bibliographical index, one of authors' names, and one of diseases, symptoms, and indications for treatment.

The Bacteriology of Every-day Practice. Medical Monograph Series, No. 2. By J. O. SYMES, M.D., D.P.H., &c. London, Paris, and Madrid: Baillière, Tindall, and Cox. 1900. Pp. 90.

THE rapid progress made in modern bacteriology, and its growing importance in medical diagnosis, renders it absolutely necessary that both practitioners and students of medicine should have, at the very least, an elementary knowledge of the methods of bacteriological investigation. In this volume the author's endeavour has been to supply a ready means for the acquisition of bacteriological knowledge, the principal objects in view being to point out in what cases bacteriological examination might help in clinical diagnosis; to describe methods of securing and identifying microscopic specimens such as the student could prepare for himself; and to give directions for taking cultures and for preserving tissues to be sent to the laboratory. We must, however, point out that, assuming as he does that the reader has no elementary knowledge of bacteriological work, the author does not begin sufficiently near the true beginning of the subject; after a few remarks on very simple apparatus, such as a platinum loop (illustrated), a pair of forceps (illustrated), and a glass pipette (illustrated), he plunges straightway into such delicate and advanced work as the staining and mounting of bacteria for microscopical examination. In the succeeding pages he deals with general infections of the blood, suppurative processes, various diseases, and concludes with an appendix on the microscope.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 2, July 9, 1900.

Combustible Gases of the Air: Air from the Sea. Existence of Free Hydrogen in the Terrestrial Atmosphere.—Armand Gautier.—From this research and previous researches on the same subject, the author concludes that pure air contains normally about $2/10,000$ of its volume of free hydrogen, to which must be added—owing to the exhalations and fermentations of the soil, vegetables, animals, or human industries—a certain proportion of hydrocarbons—which is relatively great in populous towns, small in country districts, very slight on

rocky plateaux and peaks of high mountains, and practically absent in the higher regions of the atmosphere. There still remain to be determined the nature of the hydrocarbons of the air of towns and woods and the origin of atmospheric hydrogen.

Chemical Constitution of Steel. Influence of Tempering on the State of Combination of Elements other than Carbon.—MM. Carnot and Goutal.—Continuing their researches on the chemical constitution of steel, the authors have now investigated the effect of tempering on modifying the state of combination of the various elements contained in the products of siderurgy. Their new determinations have been carried out with regard to sulphur, phosphorus, arsenic, copper, and nickel.

An Ammoniacal Chromous Sulphate.—Ch. Laurent.—The sulphates of the magnesium series give, with the alkaline sulphates, double salts of the type $MgSO_4 + K_2SO_4 + 6H_2O$. The chromous salt, of analogous formula, known at present, is the double sulphate of chromium protoxide and potassium, $CrSO_4 + K_2SO_4 + 6H_2O$, which was prepared by Peligot. The author has prepared the double ammoniacal sulphate. Owing to the fact that all the chromous salts are very easily transformed into chromic salts when in contact with air, all the experiments had to be conducted in an atmosphere of carbonic anhydride. Analysis shows the new substance to have the formula $CrSO_4 + (NH_4)_2SO_4 + 6H_2O$.

Journal de Pharmacie et de Chimie,
Series 6, Vol. xi., No. 6.

Seleniferous Sulphuric Acid.—MM. Schlagdenhauffen and Pagel.—Already inserted.

The Alteration of Syrup of Iodide of Iron and a Means of Preventing it.—M. Debraye.—The alteration of syrup of iodide of iron is due to the action of the oxygen of the air, which transforms the ferrous salt into ferric salt. To prevent this alteration it has been proposed to add a small quantity of tartaric acid; this, however, only retards the action, but does not prevent it. Formerly, syrup of iodide of iron was kept away from the light; this, however, is quite a mistake. Solutions of ferrous salts should always be put in flasks made of white glass and kept in the light, but they should at the same time be kept full and perfectly stoppered; a small quantity of tartaric acid may be added to aqueous solutions. To show the value of this treatment, the author placed in a 250 c.c. flask 1.35 grms. iodine, 0.66 gm. iron filings, 0.33 gm. tartaric acid, 330.20 grms. simple syrup. The tightly-stoppered flask was placed on a window-sill. In less than forty-eight hours all the iodide was dissolved, and the liquid took the colour of ferric salts. Gradually this colour became fainter, and in fifteen days, in winter, the syrup was as colourless as water, and the whole of the ferric iodide had passed to the ferrous state.

Eugenol, Safrol, and Propylpyrocatechin.—R. Delange.—Already noticed.

Action of Heat on Papain.—V. Harlay.—The digestive power of papain is not affected by dry heat; that is, three hours at 100° over sulphuric acid. The action of heat on papain in solution is very different, however; a temperature of 82°, under the conditions of experiment described, causing its destruction. At temperatures below 75°, the disaggregation of fibrine was complete in twenty-four hours, but at 81.5° the fragments of fibrine were only softened superficially, and at 82° the papain had no effect whatever, even after twenty-four hours.

Russian Pharmacy.—P. Jacob.—Not suitable for abstraction.

No. 7.

This number contains no matter of chemical interest.

No. 8.

Purification of Water by means of the Halogens.—F. Malméjac.—Chlorine has been used both by Traube and Bassenge for the purification of water; the latter recommended a dose of 0.0978 gm. per litre for ten minutes. Bromine, recommended by Schimburg, gave the same result with 0.04 gm. per litre, after five minutes contact. According to Allain, a dose of 1/100,000th part of iodine kills all the non-sporadic pathogenic germs in half-an-hour, as well as most of the saprophytes. The present author has carried out a systematic series of experiments with a badly contaminated water, using varying equal quantities of chlorine, bromine, and iodine per litre, taking the lowest quantity given by the above mentioned authors as the basis; that is to say, 0.01 centigram. per litre of water for half-an-hour. He found that the number of microbes per c.c. was reduced from 17,500 in the original water to 300 by the action of chlorine, to 190 by bromine, and 90 by iodine.

Detection of Benzene in Regenerated Alcohols.—G. Halphen.—For detecting the adulteration of alcohols the author has obtained very good results by forming diazoic compounds, which, conjoined with the naphthols, give oxyazoic colouring matters having so great a colouring power that their detection becomes a matter of extreme sensitiveness. The operation may be divided into five phases:—1. Separation of the hydrocarbides from the alcoholic solution. 2. Nitration of these hydrocarbides. 3. Transformation into amines. 4. Formation of a diazoic salt. 5. Conjunction with a phenol. The author then proceeds to describe the details of the operations. The higher homologues of benzene, under the same conditions, also give colouring matters which indicate their presence.

No. 9.

This number is largely taken up with the death and the funeral orations given at the funeral of the late Gustave Planchon, President of the Committee of the *Journal de Pharmacie et de Chimie*. The death of Prof. Milne-Edwards, professor of zoology at the Ecole de Pharmacie, Paris, is also announced and commented upon.

A Hydrogazometer and Urometer.—E. Benoit.—The author describes two special pieces of apparatus which, however, cannot well be understood without reference to the accompanying diagrams.

Nos. 10 and 11.

These two numbers contain no matter of chemical interest.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 6.

The Electrolysis of Chloride of Potassium.—A. Brochet.—Already noticed in this column.

The Action of Hydrogen on Selenide of Mercury and the Inverse Reaction.—H. Pélabon.—Crystallised selenide of mercury is attacked by hydrogen gas at temperatures above 400°; seleniuretted hydrogen is formed, and at the same time the mercury is set free. To study this reaction the author sealed up selenide of mercury and hydrogen in a tube, and kept them at a constant temperature for some time; they were then cooled quickly, and the gaseous mixture was analysed. After being heated to 440° for several days the gas formed smelt strongly of seleniuretted hydrogen, but the proportion of this gas was found to be never more than 0.6 per cent, no matter how long the heating had lasted. The reaction is thus limited, and this limit is due to the inverse reaction of the seleniuretted hydrogen on the mercury vapour. To show this, it suffices to maintain a sealed tube containing selenide of mercury and hydrogen at a pressure of 760 m.m. for a few minutes at a temperature of about 540°. Under these conditions it is shown that there is 15 per

cent of seleniuretted hydrogen present; but after heating for two days at 440° the proportion of seleniuretted hydrogen is reduced to 0.52 per cent.

The Composition of Essence of Sandal-wood from the East Indies.—M. Guerbet.—Already noticed in this column.

A New Gas-holder for Constant Pressures, Variable at will.—J. Riban.—The advantages claimed for this new gas-holder, which is fully explained and illustrated, are—exact constancy of flow, owing to constant hydrostatic pressure; facility of varying this pressure at will as well as measuring it; facility of completely removing all traces of air or previous gaseous residues; and facility of preventing losses of gas, or entry of air resulting from variations of the external temperature.

MISCELLANEOUS.

Preparation of Ethyldichloramine.—H. Paloma.—Ethyldichloramine has been prepared by several chemists, particularly by Tscherniak, by distilling chlorhydrate of ethylamine with chloride of lime; he has described it as an oil which can be preserved under water, and which distils at $88-89^{\circ}$. The author has also prepared it by this method, but he never succeeded in obtaining a substance which did not decompose; however, by using the dry chloride instead of using a paste of chloride of lime and water, he was successful. The purification of the product thus obtained is much more simple and the return is very good. This ethyldichloramine has been preserved under a thin layer of water in diffused daylight for eighteen months without decomposing.—*Berichte*, xxxii., p. 3343.

A New Method for the Estimation of Oxalic Acid in Urins.—E. Salkowski.—This process is based on the property possessed by oxalic acid of dissolving easily and abundantly in ether while phosphoric acid is insoluble in this liquid. Take 200–500 c.c. of urine, add 20 c.c. of HCl (sp. gr. 1.12), and shake this mixture three successive times with alcoholised ether (5 to 10 per cent of alcohol). Decant the layer of ether, filter, distil off nearly the whole of the ether, then after having added a little water, concentrate to 20 c.c. Allow to cool, and separate the resinous residue by filtration, make the solution slightly alkaline with ammonia, and add 1 to 2 c.c. of a 10 per cent solution of chloride of calcium, and acidulate with acetic acid. The precipitate of oxalate of lime thus formed is treated in the ordinary manner.—*Centralbl. f. d. Med. Wiss.*, 1899, No. 16.

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MATRICULATION EXAMINATION

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SYLLABUSES as follows are now ready, and may be obtained gratis from Messrs. CORNISH, New Street, Birmingham; or on application at the University:—

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CHARTERED INSTITUTE OF PATENT AGENTS.

The Qualifying Examination of persons desirous of being registered as PATENT AGENTS will be held in November next.

A Notice giving full particulars has appeared in the "Illustrated Official Journal" (Patents) of July 4th, 1900, and a copy of such Notice can be obtained on application to the Secretary, Chartered Institute of Patent Agents, 19, Southampton Buildings, London, W.C.

PATENTS, DESIGNS, AND TRADE MARKS ACTS 1883 TO 1888.

NOTICE IS HEREBY GIVEN, that DR.

HEINRICH VON NIEDERHAUSEN, of 7, Markkircherstrasse, Rappoltsweiler (Alsace), Germany, has applied for leave to amend the Specification of Letters Patent No. 10293 of 1899 for "A Process for Fixing Alumina or Chromic Oxide on Textile Fibres as Morants, particularly for Dyeing in Adrianople or Turkish Red."

Particulars of the proposed Amendment were set forth in the "Illustrated Official Journal" (Patents) issued on the 1st of August, 1900.

Any person, or persons, may give notice of opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

(Signed),

C. N. DALTON,
Comptroller-General.

CRUIKSHANK & FAIRWEATHER,
Chartered Patent Agents,
62, St. Vincent Street, Glasgow,
Agents.

THE CHEMICAL NEWS.

Vol. LXXXII., No. 2125.

THE SEPARATION AND ESTIMATION OF SMALL QUANTITIES OF COBALT IN PRESENCE OF NICKEL.

By THOMAS MOORE, Nouméa.

METALLIC nickel of commerce invariably contains cobalt, never, however, in large quantities, and sometimes only in that delightfully vague quantity termed traces. Up to within a few years ago it was customary in assaying to include the cobalt with the nickel; perhaps this was brought about by the facility of the electrolytic method of analysis, or perhaps by the idea that cobalt formed similar alloys to those of nickel, and might even replace it. This state of affairs, however, exists no longer, and cobalt must now be regarded as an impurity; consequently its accurate estimation becomes a necessity.

Many of the processes for the separation of the two metals, which succeed admirably when the quantity of the two metals is neither too small or disproportionate, utterly fail when applied to minute quantities of cobalt in presence of large amounts of nickel, the precipitations being either incomplete or when complete the precipitates are impure. It was therefore with the object of avoiding some of the difficulties and economising time that the process as given below was worked out.

The volumetric methods for the estimation of cobalt by titration of the higher oxides never seem to have gained confidence, owing probably to their alleged varying composition. Bailey, for example, from a series of experiments, concludes that cobalt solutions precipitated by a hypochlorite give an oxide corresponding to Co_3O_5 ; Carnot, on the other hand, maintains the formula $\text{Co}_{10}\text{O}_{16}$; whilst a whole host of text-books support the popular, but undoubtedly false, composition of Co_2O_3 . Doubtless much depends upon the mode of preparation, but enough has been said to show that there exists a certain doubtfulness as to the exact composition.

Given, however, a solution containing cobalt and nickel, nothing is gained by precipitation with bromine or chlorine and an alkali, since nickel sesquioxide is also thrown down; if, however, an emulsion of oxide of zinc is substituted for the alkali, the cobalt is precipitated almost immediately, the nickel being only thrown down to a slight extent later on and after prolonged boiling, providing always that bromine has been employed. Iodine acts similarly, but more slowly and imperfectly, whilst chlorine causes a complete precipitation of both sesquioxides. When the solution is neutral and contains no zinc salts, the decomposition takes place at ordinary temperatures; in presence of much zinc it is necessary to heat, or even boil, the solution, to obtain a complete separation. By this means it is therefore easy to concentrate the whole of the cobalt mixed with but very little nickel. Having thus obtained such a precipitate, which contains the excess of oxide of zinc, advantage is taken of the dissimilar behaviour of the two sesquioxides to peroxide of hydrogen: this instantly reduces the nickel compound to the green hydroxide, whilst the cobalt compound, whatever may have been its former composition, is now transformed into the true sesquioxide, Co_2O_3 . In actual practice the process is carried out in the following manner:—

The solution containing the chlorides of the two metals should not have much free acid, and if, as is usually the case, a little iron is present, it should be eliminated by precipitation with a slight excess of zinc oxide, and

filtered off. The filtrate is now diluted to from 300 to 400 c.c. with water, one drop of hydrochloric acid added, and raised to the boiling-point or nearly so; now add sufficient bromine water, and then not too much zinc oxide; a large excess only hinders the subsequent filtration, but is not otherwise detrimental. The solution is now boiled for about five minutes, or until the greater part of the bromine is expelled; then filter, and wash precipitate thoroughly with boiling water. The precipitate is now washed as perfectly as possible from the filter into a beaker glass, the trace adhering to the filter-paper being dissolved off by very weak hydrochloric acid containing a very little sulphurous acid; the filtrate, which need not exceed 5 c.c., being received in a capsule, evaporated to dryness, then dissolved in a few drops of water, and added to the main precipitate. The precipitate is now well boiled to thoroughly disintegrate it, and then allowed to become cold. When cold, 5 to 10 c.c. of peroxide of hydrogen, which have been rendered strongly alkaline with caustic soda, are added, the mixture well stirred, and then boiled for two or three minutes to destroy the excess of peroxide, then allowed to cool, after which it is digested for five minutes in a stoppered bottle with potassic iodide and hydrochloric acid, and the iodine thus set free titrated by means of a very weak solution of sodic hyposulphite. $1 \times 0.46511 = \text{Co}$.

The following results were obtained in presence of 2 grms. of metallic nickel perfectly free from cobalt.

Cobalt employed.	Cobalt found.
0.0001 gm.	0.00012 gm.
0.0004 "	0.00041 "
0.0008 "	0.00078 "
0.0010 "	0.00104 "
0.0020 "	0.00201 "
0.0050 "	0.00500 "

THE SPECTRUM OF RADIUM.

By EUG. DEMARCAY.

M^{ME}. CURIE has sent me a specimen of radium chloride which she believes is the purest yet prepared. The spectrum of the dilute hydrochloric solution shows the following lines:—(1). Those of the platinum electrodes. (2). A faint barium spectrum, which is reduced to the three principal lines, 4554.4, 4130.8, and 3892.2. There is also a trace of the line 4525.1. The line 4554.4 is the only well-defined one. (3). The radium lines already given in my previous paper of November, 1893 (*Comptes Rendus*, vol. cxxix., p. 716). In spite of the feeble barium spectrum and the strength of the radium spectrum, I did not observe any new line which could be attributed to radium. However, two nebulous bands, already noticed as weak nebulous lines, have considerably increased in strength. The first begins to be sharp towards 4611.9, and attains its maximum about 4627.5. It is almost symmetrical with regard to this maximum, as the band terminates about 4631.0. This and the following band (which is a little stronger), ought to be clearly visible to the eye, as it shows very distinctly in the photograph. The second band has a sharp beginning at 4463.7, and attains its maximum at 4455. The maximum continues to about 4453.4, and then the band decreases in strength very gradually, appearing to terminate about 4390.0.

The strong lines of radium are very powerful and intense in this spectrum. They are among the most intense I have ever seen, especially the lines 3814.7, 4340.8, and 4683.2.

Examination of the various plates shows that the very weak line 4364.2, which was previously considered as belonging to radium, now appears to be due to platinum ($\lambda = 4364.4$). I am also not certain that the line 4600.3 (also very weak) is due to radium, but cannot yet find to

what element it does belong. It is remarkable to note that the character of the radium spectrum, in the same way as the chemical properties of this element, approaches that of the metals of the alkaline earths.

I have not examined the visible, less refrangible portion of this spectrum with the eye, since this examination could only be performed with considerable loss of the precious material. The examination which I have made this winter, of radiferous barium rich in radium, showed very little; I only saw a single line, very ill-defined, which could be attributed to radium. This line has a wave-length approximately equal to 5665. It is only of medium strength, and very inferior to the ray 4826·3 of the same body.

As a result of this examination I think that the specimen of radium chloride in question can be considered as a little purer than former specimens when we consider the extreme sensibility of the spectrum reaction of barium. —*Comptes Rendus*, No. 4, July 23, 1900.

THE RECOVERY OF CHROMIC ACID FROM RESIDUES CONTAINING CHROMIC OXIDE.

By J. REGELSBERGER.

CHEMICAL industries, as well as that of the textile materials, consume large quantities of chromic acid, and it follows that residues containing chromic oxide are very abundant. It is not surprising, therefore, that for a long time attempts have been made to utilise these residues, especially in the manufacture of alizarine.

The bichromates are the most extensively used, especially bichromate of sodium on account of its lower price, from which salts chromic acid is liberated, either by means of sulphuric acid, or, more rarely, by means of hydrochloric acid. For this reason the greater part of the residues of oxide of chromium are met with in the form of sulphuric solutions, forming the compound commonly called chromium soda-alum.

The method used up to the present for the recovery of chromic acid consisted in precipitating hydrate of chromium, by submitting the residuary lyes to a treatment with lime or magnesia, and calcining the precipitate obtained in the presence of oxide or carbonate of calcium and carbonate of sodium. But as this process brought in its train several disadvantages, and was of relatively high cost, it was considered desirable to find a more simple and cheaper method.

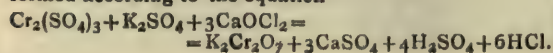
The greatest drawback of this method lay in the loss of the whole of the sulphuric acid of the residuary lyes, so that fresh quantities of sulphuric acid were necessary for the preparation of the bichromates, starting with the products of the fusion, and for their decomposition.

Haussermann (*Dingl. Polyt. Journ.*, No. 288, p. 163) removes a part of this inconvenience by oxidising the alkaline solution of chromite to the state of chromate, by means of electrolysis.

Other methods, due to Lorentz (*Zeit. Anorg. Chem.*, 1896, p. 391) and to Heibling (*French Patent*, 275, 274), utilise chrome-iron as the starting-point.

The methods of Dercum (*English Patent*, 1898, No. 3801) and Fitzgerald (*English Patent*, 1886, No. 5542) are of more interest and appear to have more practical value.

Fitzgerald proposes setting chlorine free by treating the chromic oxide with a mixture of sulphuric and hydrochloric acids, and to recover the chromic acid from the solution of sulphate of chromium thus obtained by means of the electric current. Dercum utilises the well-known reaction which takes place when we treat oxide of chromium with hypochlorite of calcium; chromic acid is formed according to the equation—



Quite recently the firm "Farbwerk vorm. Meister, Lucius, and Bruning" (*German Patent*, 103860), have published a process for treating the chromic acid lyes, without losing the sulphuric acid.

The experiments I carried out during the years 1897 and 1898, when the "Farbwerke" patents had not yet been taken out, enabled me to discover the causes to which the trouble brought about by the oxidation of the chromic acid lyes were due. These experiments, which I shall describe in detail, have shown that we may follow two different methods of electrolytic recovery,—that is to say, oxidation in alkaline solution and oxidation in acid solution.

Oxidation in Alkaline Solution.

First of all I examined the oxidising action of hypochlorite of calcium, but the results obtained by the direct action of this substance in the solid state were hardly encouraging. I then tried making the hydrate of chromium to be oxidised into a thick paste, by mixing it either with an alkaline lye, with milk of lime, or with an alkaline sulphate and milk of lime, and submitting the paste thus obtained to the action of a current of chlorine gas. I thus succeeded in oxidising almost the whole of the chromic oxide to chromic acid, but, at the same time, small quantities of hypochlorite or of chlorate were formed, and the residue generally contained a little chromic acid in the form of a calcium salt.

Although the oxidation is quite complete, it does not seem advisable, from the point of view of expense, to have to first prepare chlorine or hypochlorite of calcium. On the contrary, it is desirable to combine in one and the same operation, if possible, the preparation of the oxidising agent and the re-forming of the chromic acid.

Now the electrolysis, without a diaphragm, of solutions of alkaline chlorides is accompanied by the momentary formation of hypochlorites. When consequently, in my opinion, we simultaneously add to an electrolyte of this kind calculated quantities of hydrate of chromium and of salts of chromium, we ought finally to effect the formation of a chromate. This opinion has been fully confirmed.

By the employment of chlorides as electrolytes, we effect, by the sufficiently prolonged action of the current, the integral transformation of the oxide of chromium added into chromic acid. When, on the other hand, we use an alkaline sulphate as the electrolyte, this oxidation hardly takes place, but it becomes manifest immediately on the addition to the electrolyte of a certain quantity of chloride.

With chloride of chromium alone, metallic chromium is formed as well as chlorine. In such a case it is necessary to add a large quantity of chloride to start the oxidation.

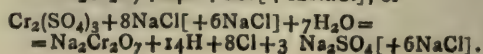
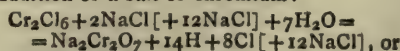
It results from this that the best effect of the current would be obtained when a nearly saturated solution of an alkaline chloride contains a quantity of oxide of chromium equivalent to the current used in the unit of time.

The chromic acid formed is always found in the form of bichromate. When the electrolyte consists of chloride of potassium, the bichromate crystallises in a state of perfect purity from a warm solution, while solutions of bichromate of sodium ought to be previously freed from the chloride of sodium which always accompany them.

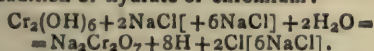
It is not astonishing that this electrolysis is always accompanied by a more or less considerable disengagement of chlorine gas, according to whether we have added to the alkali a salt of chromium or oxide of chromium.

The following equations explain the phenomena in question:—

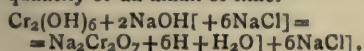
I. Addition of a salt of chromium:



II. Addition of hydrate of chromium:



III. Addition of hydrate of chromium and an equivalent quantity of an alkali or lime.



In this manner the course of the formation of chromate may be represented as follows:—The electrolysis of the solution of chloride causes the formation of hypochlorite, and this immediately oxidises the neighbouring compounds of oxide of chromium, itself changing into chloride. If there is a free base present the chromic acid is neutralised; if not, the chromic acid set at liberty decomposes further quantities of hypochlorite with the evolution of chlorine.

In reality these reactions are not produced so distinctly on account of secondary reactions taking place, such as the reduction of the hypochlorite, its electrolysis, passage to the state of chlorate, &c.

As for the intensity of the current, it should be strongest in the case of a chromium salt, less strong when hydrate of chromium is used (4.7ths of the first), and weakest in the presence of a base in quantity equal to the chromic acid (3.7ths of the first).

On account of the formation of chlorine, the anodes should be formed of some material not attacked by this element. Binoxide of lead and similar substances are not suitable for this purpose, on account of their low conductivity; carbon is strongly attacked, and gives a low return for the current used, so that we are forced to use platinum as being the most suitable.

Although the results obtained by this method are very satisfactory, the oxidation of chromic residues in acid solution offers a more simple means for the recovery of chromic acid. However, oxidation in an alkaline medium is preferable in certain special cases, as, for example, when the chromic lyes contain fairly considerable quantities of organic matter, or, again when the residues are in the solid state.

Oxidation in Acid Solution.

When we electrolyse a solution of sulphate or chloride of chromium, in an apparatus without a diaphragm, we obtain metallic chromium, and, according to circumstances, chlorine gas, but never chromic acid. In the same way, by using a diaphragm and varying the concentration, acidity, and temperature, I found it impossible to get any other result. In all these experiments I made use of platinum electrodes.

A remark made in a treatise on Mineral Chemistry, by Gmelin-Kraut, according to which oxide of chromium can be transformed into chromic acid by means of peroxide of lead in the presence of concentrated sulphuric acid, suggested to me the idea of producing the peroxide by electrolytic means, in the chromic bath itself. For this purpose I made use of lead anodes, and my attempt was crowned with success. I obtained chromic acid by electrolysing sulphate of lime, and that as easily in the presence of a diaphragm as without one. This electrolysis can be effected either hot or cold, but it is preferable to use a hot solution.

The apparatus necessary is of very simple construction. It suffices to use a vessel of lead, which serves at the same time as anode, and which holds the diaphragm formed of some reducing material, such as lead, iron, nickel, or copper.

The return I obtained from my experiments amounted to 92.5 per cent of theory, with 70 per cent of oxidising action, and to 80 per cent with 86 per cent of oxidising action; these experiments having been made with solutions of pure chrome-alum, with or without sulphuric acid as an electrolyte.

Each electrolysis is accompanied by the formation of a small quantity of white mud, composed of sulphate and

chromate of lead, and at the same time the anode becomes covered with a brownish coating, which, however, exercises no influence on the strength of the current. The power used is, according to my observations, from 8 to 11 kilowatts per twenty-four hours for 100 kilos. of bichromate of sodium. To that must be added the expense necessitated by the construction of the apparatus, and from this point of view it is especially the anodes which must be taken into account.

It is thus probable that with this new method of recovery the cost price of 100 kilos. of bichromate of sodium will not exceed the sum of 20 marks (£1), while 100 kilos. of commercial bichromate costs 54 marks (£2 14s.), without reckoning the sulphuric acid necessary for effecting the oxidation, which acid has always been lost up to the present. — *Zeitschrift für Angewandte Chemie*, p. 1123.

NOTES ON THE HYDROXIDES OF ALUMINIUM.

By E. T. ALLEN.

DURING a study of the best conditions for the precipitation of aluminium by ammonia, I became interested to know the cause of the differences in the density and other properties of the various varieties of aluminium hydroxide. Berzelius, Ramsay, and others have recorded their observations on this subject, but as their statements do not agree, it was thought best to investigate. It was found, in brief, that the composition of the precipitates formed in various ways is the same, viz., $\text{Al}(\text{OH})_3$. The amorphous varieties lose one molecule of water over sulphuric, or at 100° C. The differences, in outward appearance, in density and hygroscopicity are due therefore to differences in physical structure.

I. "Alumina U.S.P." was dissolved in hydrochloric acid, as far as possible, filtered repeatedly until nearly free from turbidity, precipitated in the cold by ammonia, allowed to stand until the precipitate settled, and then thoroughly washed by decantation with cold water.

- Air-dried (in very hot dry weather).—0.4485 gm. gave 0.1565 gm. H_2O = 34.89 per cent. Calculated for $\text{Al}(\text{OH})_3$, 34.57. (Ramsay found 45.93 per cent; *Journ. Chem. Soc.*, [2], xv., 396).
- Dried over sulphuric acid.—Prep. I., 0.2594 gm. gave 0.0926 gm. H_2O = 26.31 per cent. Calculated for $\text{Al}_2\text{O}_3\text{H}_4$, 26.09. Prep. II., 0.1323 gm. gave 0.0343 gm. H_2O = 25.92 per cent. Calculated for $\text{Al}_2\text{O}_3\text{H}_4$, 26.09. (Ramsay found 29.5 per cent; *Journ. Chem. Soc.*, [2], xv., 396).
- Dried at 100° C.—Prep. I., 0.1371 gm. gave 0.0360 gm. H_2O = 26.26 per cent. Calculated for $\text{Al}_2\text{O}_3\text{H}_4$, 26.09. Prep. II., 0.4669 gm. gave 0.1161 gm. H_2O = 24.86 per cent. (Berzelius found 35.5 per cent; "Gmelin-Kraut's Handbuch," 1874—1886, ii., Part 1, p. 619).

II. Aluminium chloride, made as in I., was precipitated by ammonia near the boiling-point, and washed thoroughly by decantation with hot water.

- Air-dried.—0.2462 gm. gave 0.0833 gm. H_2O = 33.83 per cent. Calculated for $\text{Al}(\text{OH})_3$, 34.57.
- Dried over sulphuric acid.—Prep. I., 0.2058 gm. gave 0.0545 gm. H_2O = 26.48 per cent. Calculated for $\text{Al}_2\text{O}_3\text{H}_4$, 26.09. Prep. II., 0.2977 gm. gave 0.0771 gm. H_2O = 25.90 per cent. Calculated for $\text{Al}_2\text{O}_3\text{H}_4$, 26.09.
- Dried at 100° C.—Prep. I., 0.2039 gm. gave 0.0510 gm. H_2O = 25.01 per cent. Calculated for $\text{Al}_2\text{O}_3\text{H}_4$, 26.09. Prep. II., 0.3243 gm. gave 0.0829 gm. H_2O = 25.56.

Ramsay states that the hard horny hydrate precipitated by ammonia contains 45.93 per cent water, and concludes that we have no evidence of the existence of $\text{Al}(\text{OH})_3$.

My experiments showed that the percentage of water depends upon the state of the atmosphere. The preparation I. A., at the end of a hot dry summer, had the composition $\text{Al}(\text{OH})_3$. After several weeks of rainy weather, during which the same preparation was exposed to the air, it was found to contain 36.51 per cent water instead of 34.57 demanded by $\text{Al}(\text{OH})_3$, and a third analysis made about two months later showed that the substance then contained 40.28 per cent water. Another preparation, dried under less favourable conditions than this, gave 39.65 per cent water.

It may be mentioned here that the hydroxide precipitated hot dries to a heavy powder which does not appear to be hygroscopic.

III. The hydrate of aluminium, which is formed by boiling a soluble aluminate with ammonium chloride, is, according to Löwe, much denser and more readily filtered than the precipitate by ammonia, though I have not been able to confirm this statement. Löwe (*J. B.*, 1860, 132; *Zeit. Chem.*, iii., 247), finds its composition at 100° C. is $\text{Al}_2\text{O}_5\text{H}_4$, like the other varieties of the amorphous hydrate.

IV. W. Crum (*Am. Pharm.*, lxxxix., 156), showed that soluble aluminium hydrate dried at 100° C. contained 25.67 per cent water instead of 26.09 demanded by $\text{Al}_2\text{O}_5\text{H}_4$. Our knowledge of colloidal solutions, however, does not indicate that this is a distinct variety of aluminium hydrate. Pure boiling water will dissolve a considerable quantity of any of the amorphous varieties, at least when freshly precipitated.

V. The hydroxide formed by boiling the basic carbonate with water, or better with water containing a little ammonium salt, is also the trihydrate. Basic carbonate of aluminium was prepared from pure ammonium alum by adding just enough pure caustic potash to re-dissolve the precipitate at first formed, and then saturating the aluminate solution with carbon dioxide. When this preparation was boiled with water it lost carbon dioxide and alkali. Its appearance changed entirely. It became flaky and apparently amorphous, while the basic carbonate was dense and crystalline. The preparation was washed with hot water and air-dried.

0.2393 grm. gave 0.1571 grm. Al_2O_3 .
0.4755 grm. „ 0.1642 grm. H_2O .

It was free from alkali.

	Found.	Calculated for $\text{Al}(\text{OH})_3$.
H_2O	= 34.53	34.57
Al_2O_3	= 65.65	65.43

This variety is denser and more readily washed and filtered than any of the others except VI.

VI. It has been frequently stated that the compound which carbonic acid throws down from soluble aluminates is the crystalline trihydrate of aluminium. Day (*Amer. Chem. Journ.*, xix., 707), has disproved this, and my experiments confirm his results. The crystalline precipitate formed by the slow action of water on soluble aluminates is, however, crystalline aluminium hydroxide. The following is an analysis of a preparation made by the gradual hydrolysis of potassium aluminate at the boiling temperature:—

0.5194 grm. gave 0.1804 grm. H_2O .
0.1597 grm. „ 0.1053 grm. Al_2O_3 .

	Found.	Calculated for $\text{Al}(\text{OH})_3$.
H_2O	= 34.73	34.57
Al_2O_3	= 65.93	65.43

The crystalline hydrate of aluminium is a dense crystalline powder which under the microscope was found to consist of minute transparent grains aggregated like strings of pearls. It does not, like the amorphous varieties, lose water over sulphuric acid. A preparation formed by the hydrolysis of sodium aluminate was brought to equilibrium over sulphuric acid.

0.2125 grm. gave 0.0767 grm. H_2O = 36.1 per cent.
Calculated for $\text{Al}(\text{OH})_3$, 34.57.

The dihydrate of aluminium, $\text{Al}_2\text{O}_5\text{H}_4$, is a very hygroscopic powder. It gained water persistently when kept between clamped watch-glasses in a calcium chloride desiccator. One preparation after standing several months in a glass-stoppered weighing glass, which was kept inside a balance-case, had the composition $\text{Al}(\text{OH})_3$.

The conditions under which the monohydrate, AlO_2H , forms have been already investigated by others.

Missouri State School of Mines, Rolla, Mo.

ON ELECTRIC TOUCH AND THE MOLECULAR CHANGES PRODUCED IN MATTER BY ELECTRIC WAVES.*

By JAGADIS CHUNDER BOSE, M.A., D.Sc.,
Professor of Physical Science, Presidency College, Calcutta.

(Concluded from p. 64).

Restoration of Sensitiveness to a Fatigued Substance.

It was said that the inertness of the substance, after long exposure, is due to the presence of a relatively large amount of strained B variety. It therefore follows that if by any means we can transform B into A, then after such a transformation there ought to be a restoration of the sensitiveness. It has also been stated that the B variety under ordinary circumstances is less stable than A. If now we apply a disturbing cause which is unilateral in its action—that is to say, if it converts B into A and not A into B—then such a disturbing cause will re-sensitise the fatigued substance.

Effect of Mechanical Disturbance.—Of the unilateral actions, mechanical vibration is one; for it is known that by the action of friction a substance may pass from one modification to another in one direction only. Thus the change of monoclinic into rhombic variety of sulphur is hastened by scratching with a glass rod, but the change does not take place in the opposite direction. We may now apply the crucial tests. Mechanical vibration will transform B into A, and with positive fatigued substances this ought to produce an increase of resistance (as A is less conducting than B); with negative substances the same disturbance ought to produce a diminution of resistance.

Effect of Heat.—There are other methods by which the B variety may be transformed into A; the more subtle molecular disturbance due to heat may be expected to be even more effective in producing the transformation. Here, too, the crucial test is that by slight heating the fatigued positive substance ought to show an increase of resistance, and the negative substance a diminution of resistance. The two following curves (Figs. 8 and 9) confirm in a remarkable manner my anticipations.

Effect of Heat and Mechanical Disturbance on a Positive Fatigued Substance.—I shall at first deal with the curve for iron. At the end of No. 6 curve, the substance was left in the inert stage b. While in this state, the receiver was heated to a slight extent. Observe in the dotted portion of the curve the sudden fall of conductivity (increase of resistance). I should like to say here, that, though the fall has been indicated by a straight line, as representing the somewhat sudden fall of conductivity, I sometimes noticed on careful inspection a slight oscillatory movement of the galvanometer spot during this process. The significance of this I will notice on a future occasion. The ultimate effect of slight heating (excess of heat produces other complications) is the restoration of the original reduced conductivity. If the application of heat transforms B into A, we may expect the substance to regain its sensitiveness, which it lost in the fatigued state stage b. The receiver was now exposed to radiation, and it at once responded, exhibiting almost its original sensibility. Observe how the subsequent portion of the curve

* A Paper read before the Royal Society, February 8, 1900.

is a repetition of the curve No. 6, and how the substance arrives at the second fatigued state b' . To observe the effect of mechanical disturbance a gentle tap was given to the receiver, and at once there was produced an increase of resistance due to the transformation of B into A, the receiver regaining its sensitiveness by the transformation. The action of radiation was continued, and after a few reversals the substance once more arrived at the third fatigued state b'' . The process described above could be repeated any number of times.

Effect of Heat and Mechanical Disturbance on a Negative Fatigued Substance.

Experiments similar to the above were carried out with an arsenic receiver. From the curve given below (Fig 9) it is seen that the reaction of the negative substance is in every respect opposite to that of a positive substance. It will be noticed that the same cause—i.e., heating or tapping—produces, as necessary consequences of the hypotheses previously stated, two opposite reactions in the two classes of substance. I have been able to verify this deduction by observations with nearly a dozen different substances, and have not, so far, come across any to contradict it. It thus appears that tapping restores the sensitiveness not by the separation of the electrically-welded particles (in which case tapping ought to have

reality. The investigation of this aspect of the subject has given me some extraordinary results; they seem to connect together many phenomena which at first sight do not seem to have anything in common. Another interesting question, the consideration of which has for the present to be postponed, is, why is it that the sensitiveness is so marked in discontinuous metallic particles? In other words, why is the phenomenon mainly one of skin or *twach*? Is the phenomenon wholly unknown in continuous solids?

The experiments described in the present paper show:—

- (1). That ether waves produce molecular changes in matter.
- (2). That the molecular or allotropic changes are attended with changes of electric conductivity, and this explains the action of the so-called coherers.
- (3). That there are two classes of substances, positive and negative, which exhibit opposite variations of conductivity under the action of radiation.
- (4). That the production of a particular allotropic modification depends on the intensity and duration of incident electric radiation.
- (5). That the continuous action of radiation produces oscillatory changes in the molecular structure.
- (6). That these periodic changes are evidenced by the corresponding electric reversals.

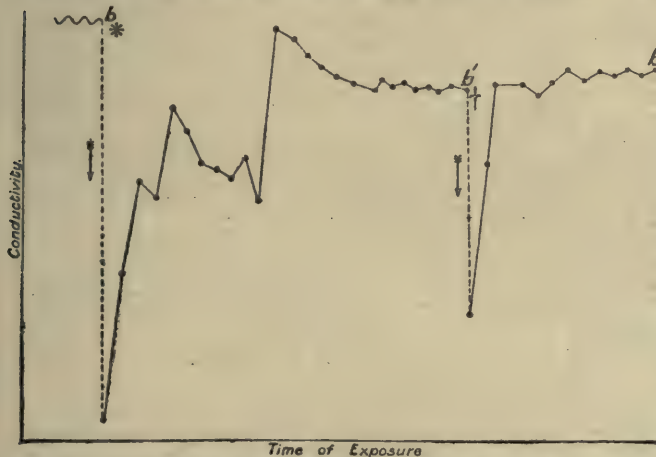


FIG. 8.—CURVE SHOWING THE EFFECT OF HEAT AND MECHANICAL VIBRATION ON A FATIGUED IRON-FILINGS RECEIVER.

* Application of heat.

+ Application of a tap.

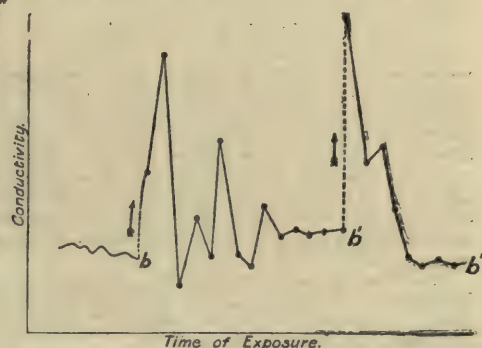


FIG. 9.—CURVE SHOWING THE EFFECT OF HEAT AND MECHANICAL VIBRATION ON A FATIGUED ARSENIC RECEIVER.

* Effect of heat.

+ Effect of tapping.

produced an increase of resistance in *both* the classes of fatigued substance), but by removing the strain in B and thus converting it into A.

The effect of electric radiation is thus to produce rearrangement of atoms and molecules in a substance; so does light produce new atomic and molecular aggregation in a photographic plate—a subject to be dealt with in detail in a future paper. Some of my audience at the Royal Institution (January, 1897) may remember my attempt at explaining the action of the so-called coherers (which, perhaps, may be better described as “molecular receivers”) by analogy with the photographic action. I had then no proofs for the assertion. I have since been able to obtain experimental evidence that the two phenomena are identical. The coherer may therefore be regarded as a linear photographic plate; since we are more likely to understand the complex photographic action from the consideration of the much simpler action of electric radiation on elementary substances, where the effects are not complicated by secondary reactions, a photographic plate may be regarded as merely an assemblage of “molecular receivers.” I hope also to prove that nearly all the detectors of radiation are molecular receivers in

(7). That the “fatigue” is due to the presence of the “radiation product,” or strained B variety.

(8). That by means of mechanical disturbance or heat, the strained product can be transformed into the normal form, and the sensitiveness may thereby be restored.

The method described above of detecting molecular changes is extraordinarily delicate, and is full of promise in many lines of inquiry in molecular physics. It is also seen that the phenomenon of contact sensitiveness, contrary to previous suppositions, is perfectly regular. There is no capriciousness in the response of sensitive substances to the external stimuli, which may be mechanical, thermal, or electric. The curves given above show it; but they fail to give a fair idea of the richness and variety of the molecular phenomena, seen as it were reflected in the fluttering galvanometer spot of light; of the transitory variations, of the curious molecular hesitation at critical times as to the choice of the structure to be adopted, and of the molecular inertia by which the newly-formed structure is carried beyond the position of stability, and the subsequent creeping back to the more stable position. The varieties of phenomena are unlimited, for we have in

each substance to take account of the peculiarity of its chemical constitution, the nature of its response to ether waves, the lag and molecular viscosity. All these combined give to each substance its peculiar characteristic curve; it is not unlikely that these curves may give us much information as to the chemical nature and the physical condition of the different substances. I am at present trying to arrange an apparatus which will by means of the pulsating galvanometer spot of light, automatically record the various molecular transformations caused by the action of external forces.

Before concluding, I take this opportunity of expressing my grateful acknowledgments to the Royal Society for the encouragement I received from the Society for the last five years during which investigations on "Electric Radiation" have been in progress at the Presidency College. I may say that the difficulties have been very numerous and disheartening, and that without this encouragement the work which it has been my good fortune to carry out would in all probability have remained unaccomplished. The Government of Bengal has also been pleased to evince a generous interest in these investigations. My assistant, Mr. Jagadindu Ray, and my pupils, Messrs. P. K. Sen, B.A., and B. C. Sen, B.A., have rendered me active assistance].

THE REFRACTOMETRY OF MINERAL WATERS.

By Dr. E. RIEGLER.

Up to the present time, no special study has been made of the refractive indices of mineral waters. The index of refraction of a solution depends on the nature and the quantity of the salts it contains; this index should therefore be an important character of mineral waters.

Before entering into the details of this work, it is advisable to point out that the index of refraction of a solution varies inversely with the temperature, and, further, that it varies with the adjustment of the refractometer.

To obviate these inconveniences, and to obtain figures independent of the temperature at which the operation is carried out, and of the adjustment of the apparatus, we proceed in the following manner:—

1. We first determine the index of refraction of the mineral water at the temperature shown by the thermometer placed in the cylinder of a Pulfrich refractometer; let N be this index.

2. We then determine the index of distilled water at the same temperature; let n be this index.

The results of this research show that the difference ($N-n$) is independent of the temperature at which the observations are made and of the adjustment of the apparatus. A few examples will demonstrate this fact.

Water from Marienbad (Kreuzbrunnen) at a temperature of 17° has a refractive index $N=1.33500$; distilled water at the same temperature has an index $n=1.33336$. By determining the indices of these same waters at a temperature of 12° , we obtain $N=1.33533$ and $n=1.33369$. The difference of $N-n$ at 17° and at 12° is the same; that is to say, 0.00164 .

The most practical refractometer for the determination of the indices of mineral waters is that of Pulfrich; this apparatus will give very exact readings to the fifth place of decimals inclusive.

The temperature is indicated by a small thermometer placed in the glass cylinder containing the mineral water.

The divisions of the refractometer are marked in degrees, which can be transformed into the index of refraction by the aid of a table accompanying the instrument.

The determination is made with a sodium flame, either with a Bunsen burner or Barthel spirit flame.

To determine the relation which exists between the index of refraction and the fixed residue of the mineral water under examination, we evaporated about 100 grms. on a water-bath, then dried the residue at $100-105^{\circ}$ until the weight was constant, and calculated the result for 1 litre.

We can see from the accompanying table that a constant relation exists between the fixed residue of different waters and the index of refraction. It is evident that a knowledge of this index will serve to characterise mineral waters, and thus may be used for their estimation, the more so that these determinations only require a few minutes to perform.

In the accompanying table we have arranged the waters examined according to the amount of their index of refraction. — *Buletinul Societatii de Stiinta d. Bucuresti Romania*, Year ix., Nos. 2-3, p. 251.

ACCIDENTAL IMPURITIES OF CARBIDE OF CALCIUM.

By FELIX B. AHRENS.

In various samples of carbide from different sources we find large metallic morsels which have been identified as ferro-silicon or silico-carbide of iron. The high proportion of iron in this substance precludes the idea that it is due to impurities in the coke or the lime; it appears rather to be due to the fusion of the metallic clips serving

Table of Mineral Waters Examined from the point of view of their Index of Refraction.

Name of the mineral water.	Temperature.	Index of refraction of mineral waters, N .	Index of refraction of distilled water, n .	Difference between these indices ($N-n$).	Total solid matter in 1000 grms.
1. Eaux-Bonnes	16	1.33369	1.33344	0.00025	0.6621
2. Mont Dore	17	1.33369	1.33336	0.00033	1.3900
3. Caciulata	13	1.33402	1.33361	0.00041	1.8100
4. Ems-Krähnen	17	1.33402	1.33336	0.00066	2.8372
5. Borseck	16	1.33418	1.33344	0.00074	2.9900
6. Wildungen (Helen-Quelle) ..	16	1.33418	1.33344	0.00074	3.3380
7. Niederselters	18	1.33402	1.33328	0.00074	3.3730
8. Billiner-Saurbrunn	18	1.33418	1.33328	0.00090	4.1400
9. Slanic	17	1.33427	1.33336	0.00091	4.9380
10. Karlsbader Sprudel	17	1.33434	1.33336	0.00098	5.4900
11. Karlsbader Mühlbrunnen ..	18	1.33418	1.33328	0.00090	5.5000
12. Vichy-Hôpital	16	1.33451	1.33344	0.00107	5.1750
13. Vichy Grande-Grille	17	1.33443	1.33336	0.00107	5.0530
14. Kissingen-Rakoczi	18	1.33484	1.33328	0.00156	8.7290
15. Marienbad-Kreuzbrunnen ..	17	1.33500	1.33336	0.00164	8.9600
16. Hunyadi Janos	18	1.34003	1.33328	0.00675	43.1100
17. Breazu	19	1.34173	1.33320	0.00853	55.8870
18. Carabana	18	1.34475	1.33328	0.01147	75.3270
19. Rubinat	17	1.34692	1.33336	0.01356	100.8700

as holders for the electrode, and this fact seems to indicate a considerable consumption of the electrodes. This inconvenience is, as a rule, due to the faulty construction of the furnace, inasmuch as it allows too great a consumption of the electrodes, or else does not allow of good regulation. It is extremely improbable that this ferro-silicon is due to a mistake in the manufacture, as it is very frequently found in commercial carbide of calcium.

A short time ago I found in a carbide of calcium some of these metallic morsels, a few of which were several c.m. in diameter, and I was able to collect a certain quantity. They contained not only iron and silicon, but also a large proportion of copper. It may easily be imagined that this latter metal came from the conducting-wires and fell into the furnace after a short circuit. This silicide had a crystalline fracture, was fairly friable, and strongly resistant to chemical reagents. Boiling hydrochloric acid had absolutely no action on it, and boiling aqua regia very little. Of a piece weighing 0.5 gm. only 0.1382 gm. was dissolved after boiling three days with this latter reagent. The alkalis and alkaline carbonates attack it very easily when fused.

To effect its analysis we begin by breaking up a few pieces taken at random, in a steel mortar, and then pulverise them in an agate mortar; the powder is then fused with the double carbonate of potash and soda; during this operation a mass of green flames is given off.

We can never manage the complete disaggregation of the silicide in one operation, even after maintaining the fusion for several hours; it is necessary to submit the silica separated by means of hydrochloric acid to the same treatment once or twice more. After completing the operation in the ordinary manner, by making the silica insoluble by means of hydrochloric acid in the presence of a small quantity of chlorate of potash, we precipitate the iron by a large excess of ammonia, so that the copper will remain in solution. The oxide of iron is re-dissolved and re-precipitated three times under the same conditions to get it absolutely free from copper. Finally the copper itself is precipitated by means of sulphuretted hydrogen in hydrochloric solution.

As the silicide contains carbon, this latter is estimated by combustion in a current of oxygen.

0.1595 grm. of silicide gave—

0.006 grm. CO_2 = 1.03 p.c. C.

0.4016 grm. of silicide gave—

0.2362 grm. SiO_2 = 27.61 „ Si
0.3384 „ Fe_2O_3 = 58.96 „ Fe
0.654 „ Cu_2S = 12.76 „ Cu

100.36 p.c.

We found certain differences on examining the physical properties of various morsels of silicide; some were of a grey colour, and others, more numerous, were slightly red. The first had a hardness of 8 to 9, and were friable and easily powdered; the second had a hardness of 7 to 8, and were more coherent. Finally we met with a small quantity of flattened cakes, grey in the interior and bright yellow on the surface.

These three different substances were analysed by the method described above, and found to have different compositions. The grey portions with the hardness 8 to 9 contained—

0.2642 grm. of the material gave—

0.1884 SiO_2 = 27.00 per cent Si
0.2288 Fe_2O_3 = 60.62 „ Fe
0.0154 Cu_2S = 4.66 „ Cu
0.0186 $\text{P}_2\text{Mg}_2\text{O}_7$ = 1.97 „ P

The remainder consisted principally of carbon.

The analysis of the reddish pieces gave the following results:—

0.6682 grm. of the material gave—

0.3436 SiO_2 = 24.00 per cent Si
0.4924 Fe_2O_3 = 51.58 „ Fe
0.1988 Cu_2S = 23.76 „ Cu
Remainder = 0.66 „ C

As for the flattened cakes, they were analysed after being powdered and thoroughly mixed, and gave the following results:—

0.3475 grm. of the material gave—

0.1453 SiO_2 = 19.6 per cent Si
0.2904 Fe_2O_3 = 58.5 „ Fe
0.0956 Cu_2S = 21.9 „ Cu
100.0 „

—Zeit. für Angewandte Chemie, May 1, 1900.

ANALYSIS OF THE MINERAL WATER FROM THE COLD OR "PARC" SPRING AT EVAUX-LES-BAINS (CREUSE).

By EDMOND BONJEAN.

The mineral water springs at Evaux-les-Bains are as a rule thermal; their temperature is 56° (César), 54° (Desglades), 52° (Bain de Vapeur), and 39° (Bassin Rond). These temperatures were taken by M. Picaut in February, 1900. The temperature of the air at the time was 12°.

Recent excavations have shown the existence of this new spring. Like most mineral springs from a common source, the different springs at Evaux come from the same thermal fissure, form several branches during their passage through the ground, and give rise to several outfalls of different temperatures; this is caused by the cooling undergone by each stream of water during its circulation through the more or less elongated subterranean passages connecting the principal thermal fissure with the surface of the ground.

There is a strong resemblance between the results of the analysis I have made of the water from the cold spring and the results of the analyses made in 1877, at the labora-

Results of the Analyses.—Samples taken December 28, 1899.

The results are given in grms. per litre.

1. Elementary Analysis.

Silica, SiO_2	0.0990
Oxide of iron	traces
Oxide of manganese	traces
Alumina, Al_2O_3	traces
Lime, CaO	0.0728
Magnesia, MgO	0.0090
Soda, Na_2O	0.5498
Potash, K_2O	0.0339
Lithia, Li_2O	0.0020
Ammonia	traces
Sulphuric acid, SO_3	0.5001
Chlorine, Cl	0.1214
Total carbonic acid	0.2402
Arsenic	0.00025
Fluorides	distinct traces
Nitrates, nitrites, iodine	none
Oxygen absorbed from per- manganate of potash	Acid sol. 0.0035 Alkaline sol. 0.0035
Residue at 110—120°	1.492
Residue after incineration	1.421
Loss at red heat	0.071
Sulphuric residue	1.550
Total hydrometric degree	21.5°
Permanent hydrometric degree	2.0°
Alkalinity, as CO_3Na_2	0.2968

tory of the School of Mines, of the various thermal waters of Evaux. I have detected rare substances which were not noticed in these former analyses, amongst them being lithium, arsenic, manganese, and fluorine, which are of great therapeutic interest.

The fluorine was detected in 10 grms. of residue (from about 6.5 litres) attacked by pure sulphuric acid, and the products of distillation collected in distilled water. The presence of fluoride of silicon was shown by the production of gelatinous silica on contact with water.

The residue from the water is fairly rich in silica (99 m.grms. per litre), so that it is unnecessary to add silica before treating with sulphuric acid.

The alkalis (soda, potash, lithia) were separated and estimated by the method I have already described (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 691). The lithia was weighed in the state of phosphate, Li_3PO_4 . The arsenic was estimated in Marsh's apparatus on 10 grms. of the residue.

The iodine, tested for by Armand Gautier's method (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 456), gave only negative results on 10 grms. of residue.

It should be noted that this water does not contain any free carbonic acid, the whole being saturated with the alkaline earths, the soda and lithia, in the state of bicarbonates.

II. Arrangement of Fixed Elements.

Free silica, SiO_2	0.0990
Carbonate of lime, CO_3Ca	0.1300
Carbonate of magnesia, CO_3Mg	0.0189
Carbonate of soda, CO_3Na_2	0.1350
Sulphate of soda, SO_4Na_2	0.8363
Sulphate of potash, SO_4K_2	0.0627
Chloride of sodium, NaCl	0.2001
Carbonate of lithium, Li_2CO_3	0.0048
Arsenate of soda, AsO_4Na_3	0.0007
Fluorine, alumina, ferrous and manganous carbonates	traces
Total fixed elements	1.4875
Residue at $110-120^\circ$	1.4920

III. Probable Combination of the Elements Found in the Water.

Free carbonic acid	none
Sulphate of soda, SO_4Na_2	0.8363
Sulphate of potash, SO_4K_2	0.0627
Chloride of sodium, NaCl	0.2001
Bicarbonate of soda, NaHCO_3	0.2138
" lime, $\text{CaCO}_3\cdot\text{CO}_2$	0.1872
" magnesia, $\text{MgCO}_3\cdot\text{CO}_2$	0.0287
" lithia, LiHCO_3	0.0076
" iron	traces
" manganese	traces
Free silica, SiO_2	0.0990
Alumina, Al_2O_3	traces
Arsenate of soda, AsO_4Na_3	0.0007
Fluorides	distinct traces
Organic matter (as oxygen)	0.0035
Ammoniacal salts	traces
Organic nitrogen	traces
Total matter in solution	1.6396

—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 10.

Action of Reduced Nickel on Acetylene.—Paul Sabatier and J. B. Senderens.—The authors continue their research on the hydrogenation of acetylene in presence of nickel, cobalt, reduced iron, or platinum black, and now prove that, in contact with a column of these metals, maintained at a suitable temperature, the hydrogen produced by the destructive reaction acts on the excess of acetylene.—*Comptes Rendus*, cxxxi., No. 3.

ESTIMATION OF ALKALI CARBONATES IN THE PRESENCE OF BICARBONATES.*

By FRANK K. CAMERON.

(Concluded from p. 69).

Two series of titrations were then made with the potassium carbonate solution. In the first series, the potassium carbonate solution was heated to boiling in each case before titrating. In the second series, in each case the solution was filled with crushed ice and shaken until the temperature was lowered to less than 1°C . before titrating. The number of c.c. of the acid sulphate solution required to neutralise 1 c.c. of the potassium carbonate solution was—

At 0° to 1°C	1.455 c.c.
At room temperature (about 26°C .)	1.262 "
After boiling (about 97°C .)	1.210 "

From these results it would appear that the reaction was more complete at the higher temperature, in spite of the fact that the inversion of the acid potassium carbonate is more rapid at these higher temperatures and might be expected to produce exactly opposite results. For instance, the solutions which had been titrated at 97° were very strongly coloured within five minutes after the titration was completed, while those which were titrated at 1° showed only a faint pink colour after standing for upwards of an hour. The true explanation of the results, however, became apparent in the course of these titrations. It was found that it takes a measurable time for the reaction between the acid sulphate and carbonate to run to end, and that if the acid sulphate is delivered too rapidly from the burette a considerable excess may be run into the carbonate solution before the colour of the indicator disappears, so that, with these two effects of inversion of the acid carbonate and the relatively slow reaction velocity between the carbonate and acid working against each other, it would be possible to run in the solution at such a rate as to obtain any desired result within quite wide limits, and, in fact, beautifully comparable results were thus obtained. The value of the method would be very slight if the personal equation could not be eliminated in the titrations. That this can be done, however, was clearly demonstrated. If the acid potassium sulphate solution is delivered from the burette at about the rate of two drops per second, and the vessel containing the alkaline carbonate is constantly and vigorously shaken, markedly lower reading will be obtained than by any other procedure; furthermore, the readings thus obtained were found to be quite independent of the temperature at which the titrations were made. These facts were confirmed by several long and satisfactory series of titrations. This point having been clearly established, a solution of sodium carbonate was carefully prepared and boiled for some time to complete the inversion of any acid sodium carbonate which might be present. After being cooled to room temperature and made up to the desired volume, it was titrated with the following results:—The first column represents the amount of carbonate, the second column the amount of acid sulphate, and the third column the ratio of the readings:—

TABLE III.

20.00	21.50	1.075
20.00	21.60	1.080
30.00	32.30	1.076
30.00	32.30	1.076

1.077

The sodium carbonate solution was then analysed by boiling with an excess of acid potassium sulphate and titrating the excess of acid with a solution of potassium

* Contribution from the Division of Chemistry, U S. Department of Agriculture. From the *American Chemical Journal*, vol. xxiii., No. 6.

hydrate of known concentration. The results are here given:—The first column indicating amounts of carbonate taken, the second column amounts of acid potassium sulphate, and the third amounts of potassium hydrate required to neutralise the excess of acid:—

TABLE IV.

20'00	50'00	5'50
20'00	50'00	5'50
20'00	50'00	5'50
20'00	50'00	5'50
		5'50

1'00 c.c. KOH solution = 1'352 c.c. HKSO₄ solution.

5'50 " " = 7'436 " "
20'00 " Na₂CO₃ " = 43'564 " "
1'00 " " " = 2'128 " "

But since only one-half as much acid potassium sulphate would be required to convert the carbonate to acid carbonate, 1 c.c. of the Na₂CO₃ was equivalent to 2'128 c.c. ÷ 2 or 1'064 c.c. of the HKSO₄ solution. Comparing the value found by direct titration, 1'077 c.c., the error for 1 c.c. was about 1'2 per cent. More accurate results have, however, been obtained for both sodium carbonate and potassium carbonate. This error would amount to 0'10 c.c. in reading for 10 c.c., about 0'25 c.c. for 20 c.c., or nearly 0'50 c.c. in reading a titration of 30 c.c. But it has been shown repeatedly that readings for this amount could be obtained by different observers agreeing to within less than 0'20 c.c., and it may be said that the probable error for such an amount is certainly no greater than this. Considering the number and nature of the operations involved, the agreement obtained above was considered satisfactory, and it was not deemed worth while to repeat the work merely for the purpose of being able to present more refined figures.

In order to demonstrate that the presence of sodium bicarbonate in the salt analysed does not affect the accuracy of the method, mixtures of the carbonate and bicarbonate were prepared. Before titrating these mixtures with the acid potassium sulphate solution, the solutions of the carbonate and bicarbonate were separately titrated with this reagent. In Table V. the first column represents amounts of sodium carbonate taken, the second column the amounts of acid potassium sulphate required to neutralise them respectively, and the third column the ratio of the readings:—

TABLE V.

10'00	8'90	0'890
20'00	17'50	0'875
30'00	26'30	0'876
15'00	13'29	0'886
10'00	8'90	0'890
20'00	17'60	0'880
20'00	17'60	0'880
30'00	26'45	0'882
30'00	26'45	0'882
30'00	26'45	0'882
		0'882

A solution of sodium bicarbonate was then prepared and allowed to stand until equilibrium had been reached with the inverted normal carbonate. It was then titrated with the results here given:—

TABLE VI.

25'00	14'60	0'586
10'00	5'90	0'590
10'00	6'10	0'610
10'00	6'10	0'610
20'00	12'30	0'615
		0'602

Mixtures were then made by adding 10 c.c. of the sodium bicarbonate solution to 20 c.c. of the normal

sodium carbonate solution and titrating as before. The first column represents the amount of acid potassium sulphate solution required, the second column gives the reading corrected for the sodium bicarbonate added, and the third column the corresponding amount of acid required to neutralise 1 c.c. of the sodium carbonate solution taken:—

TABLE VII.

23'70	17'68	0'884
23'75	17'73	0'886
23'70	17'68	0'884
		0'885

The agreement of this figure, 0'885, with that found in Table V., 0'882, is very satisfactory, and may be regarded as establishing the point under investigation. It should be remembered, however, that when sodium carbonate is added to a solution containing sodium bicarbonate—and consequently some inverted carbonate—the equilibrium between the two substances may well be materially altered. In solutions as dilute as those examined, this displacement was probably very small, and so did not interfere with the demonstration of the fact that the presence of acid sodium carbonate does not interfere with the estimation of the hydrolysed sodium in the solution. But when the concentrations are considerable, this equilibrium displacement may well become an important factor. Should this method ever commend itself to use in technical work, this displacement of the equilibrium corresponding to an apparent increase of the amount of normal carbonate present on dissolving mixtures must be considered.

An interesting extension of the method has been developed in the course of our work. It is frequently necessary to make a rapid determination of the chloride as well as the carbonates in solution. This may be done in the following way:—As soon as the solution containing the carbonate has been titrated to neutral action with acid potassium sulphate, a drop or two of this reagent is added in excess to retard the inversion of the bicarbonate to the normal alkaline carbonate. A small amount of a solution of potassium or ammonium chromate is then added as an indicator, and the solution titrated at once with a standard solution of silver nitrate. Before titrating with the silver nitrate the solution may be boiled, in which case the inverted carbonate must again be neutralised before making the determination for the chloride. But little advantage is gained thereby, however, and results in every way satisfactory have been repeatedly obtained, working throughout at the room temperature. For instance, a solution (tenth normal) of sodium carbonate was prepared by standardising against a tenth normal (N/10) solution of acid potassium sulphate; also a solution of sodium chloride, 1 c.c. of which was equivalent to 1'734 c.c. of a tenth normal solution of silver nitrate. The following are the results obtained with the mixtures of the sodium carbonate and sodium chloride solutions. The first column represents amounts of sodium carbonate taken, the second column represents the amounts of sodium chloride taken, the third column the amounts of acid potassium sulphate required to neutralise the mixtures, and the fourth column the amounts of silver nitrate required to precipitate the chloride present:—

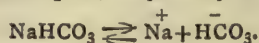
TABLE VIII.

5'00	10'00	5'05	17'35
10'00	10'00	10'10	17'35
15'00	10'00	15'20	17'35

The agreement shown in these results leaves nothing to be desired, and many more equally satisfactory determinations have been made. An interesting theoretical point is involved in the operation just described. The presence of normal carbonates in the solution would, it is well known, interfere with a titration for chloride with silver nitrate, as insoluble silver carbonate would be

formed to some extent and interfere with the desired precipitation of the chloride. The reaction is to be regarded

as the result of the silver ions Ag^+ coming in contact with the carbonic acid ions CO_3^{+} . But no such reaction is to be observed in the case we have been discussing, where acid sodium carbonate is in the solution. Therefore it appears reasonable to assume that acid sodium carbonate does not yield a CO_3^- ion, but probably dissociates, thus—



and the ion HCO_3^- does not react with the silver ion to give an insoluble compound. There is further evidence to support this view. (Walker and Cormack, *Journ. Chem. Soc.*, 1900, xlvii., 5; "Foundations of Analytical Chemistry," Ostwald and McGowan, pp. 193 and 207).

If a solution of acid sodium carbonate is added to a solution of a barium salt there is only a little precipitate formed at first, though the precipitation of the barium generally proceeds and is completed in time; more quickly if the solution be heated. It has been shown that acid sodium carbonate in water solution is unstable, some normal carbonate being formed at once, and it is to this small amount of normal carbonate that the first precipitation of the barium is due. But when this has taken place the equilibrium between the sodium carbonate and acid sodium carbonate is destroyed, more sodium carbonate is formed, and the precipitation of the barium again proceeds. This action is, of course, continuous. As the inversion of the acid sodium carbonate is more rapid at high temperatures, the formation of the normal carbonate and subsequent precipitation of the barium will proceed more rapidly on heating.

The use of ammonium carbonate in precipitating insoluble carbonates seems worthy of consideration in this connection. Unlike the corresponding sodium and potassium salts, ammonium carbonate is unstable in water solution, breaking down with the formation of the acid carbonate and the escape of some of the ammonia as such. But an equilibrium is established between the normal carbonate and the acid carbonate, which is destroyed when the solution is brought into contact with some salt which will precipitate an insoluble carbonate, such as calcium or barium. The inversion of the acid carbonate is measurably slow, however, and, as is well known, to obtain complete precipitation the solution must be allowed to stand for some time or be heated.

A statement of some of the preliminary experiments on the inversion phenomena referred to may be of interest in this connection. Three portions of a sodium carbonate solution were titrated with acid potassium sulphate to loss of colour with phenolphthalein as indicator, allowed to stand for twenty-four hours, and then titrated a second time to loss of colour. The results are here given, the first column being amounts of the carbonate solution, the second column amounts of acid sulphate added, and the third column amounts of acid sulphate required to neutralise the solution after standing.

TABLE IX.

10'00	8'90	1'00
20'00	17'50	1'85
30'00	26'30	2'55

It would appear that the inversion was approximately proportional to the initial amount of the bicarbonate, but as the concentrations were not quite the same and the sulphates present may have an influence, this conclusion can only be drawn tentatively. Some measurements, which have been made by Mr. Lyman J. Briggs, indicate that the inversion at first approaches a maximum quite rapidly, but, when equilibrium has been nearly reached, it becomes very slow and probably requires a long time before reaching final equilibrium.

Three portions of 20 c.c. of a potassium carbonate solution were each titrated to disappearance of alkaline reaction with 24'2 c.c. of the acid potassium sulphate solution, and, after standing forty-eight hours, each required 3'1 c.c. of the acid sulphate solution to neutralise them.

Ten c.c. of a sodium silicate solution required 14'1 c.c. of the acid sulphate solution to neutralise it. It was immediately boiled for three minutes, after which it required 1'1 c.c. of the acid sulphate solution to neutralise it; another portion of 10 c.c., to which 14'1 c.c. of the acid sulphate had been added after the expiration of an hour, at the room temperature, required 0'9 c.c. to neutralise it. The case of the sodium bisilicate differs essentially, however, from that of the sodium bicarbonate, in that no volatile component can be formed. So that this apparent inversion must be more limited in amount, and is in reality a measure of the hydrolysis of the salt. It was not appreciable in the case of the borates or phosphates, as has already been noted.

An application of the method to a solution of sodium silicate was made. Table X. gives the results of the titrations of the solution with the acid potassium sulphate, the first column indicating amounts of the silicate solution, the second column amounts of the acid sulphate, and the third column the corresponding ratios:—

TABLE X.

20'00	31'00	1'550
20'00	31'00	1'550
10'00	15'70	1'570
10'00	15'80	1'580
10'00	15'50	1'550
10'00	15'70	1'570
15'00	23'60	1'573
15'00	23'60	1'573
20'00	31'40	1'570
20'00	31'45	1'572

1'566

The solution was then analysed by adding an excess of hydrochloric acid, boiling, and titrating the excess of the acid with a solution of potassium hydroxide. The first column of Table XI. indicates the amounts of silicates taken, the second column the amounts of hydrochloric acid added, and the third column the amounts of potassium hydrate required to neutralise the excess of acid:—

TABLE XI.

40'00	20'00	11'70
40'00	20'00	11'70
40'00	20'00	11'70

11'70

Since in this case the silicic acid does not escape from the solution as does carbonic acid, when the hydrochloric acid is added to excess, enough potassium hydrate will be required not only to neutralise the excess of hydrochloric acid, but also to re-convert the silicic acid to potassium bisilicate before the solution will be alkaline.

20'00 c.c. HCl solution = 20'928 c.c. KOH solution.

Excess of " " = 11'700 " "

40'00 c.c. sodium silicate " " " " = 9'228 " "

1'00 c.c. sodium silicate " " " " = 0'231 " "

It has been shown that 1 c.c. KOH solution was equivalent to 6'764 c.c. H_2SO_4 solution; therefore 0'231 c.c. KOH solution was equivalent to 1'562 c.c. H_2SO_4 solution. The agreement of this figure 1'562 c.c. with that given in Table X., 1'566 c.c., must be regarded as entirely satisfactory.

Summary.

The principal results of this investigation may be summarised as follows:—

1. The amount of a soluble alkaline carbonate in a solution can be quickly and accurately determined whether the bicarbonates are present or not.

2. The method seems well adapted to the estimation of silicates, borates, phosphates, and the salts of weak acids in general.

3. The bicarbonates are unstable in water solution, and are more or less completely converted into the normal salt.

4. Alkaline bicarbonates are themselves neutral in water solutions; they do not yield a CO_3 ion by hydrolysis, or they do so only to a slight extent.

5. Therefore, an accurate volumetric determination of chlorides by means of a standard silver nitrate solution is feasible in the presence of alkaline bicarbonates, if the hydrolysis of these latter is prevented.

NOTICES OF BOOKS.

Physics: Experimental and Theoretical. In Two Vols. By R. H. JUDE, D.Sc., M.A., and H. GOSSIN. London: Chapman and Hall. Vol. I. Pp. 926.

THIS work is based upon a book by Prof. Gossin, of Lyons, and has been translated and considerably amplified by Dr. Jude, who is responsible for its present form.

The first volume is divided into three sections, and treats of Mechanics, Hydrostatics, Pneumatics, Heat, and Acoustics, and is intended for use in the senior classes of science and technical schools. The general plan of the work is the same as that followed in Ganot's and Deschanel's "Physics," though a great deal of historical matter has been superseded in favour of more modern material.

It is a matter for regret that Dr. Jude did not devote more time to correcting and revising his proofs, for he has committed himself to several statements which, to say the least, are open to question, especially in the earlier part of the book. For instance, on page 11 we read: "The external force causing the body to travel in a curve must always be in the direction of the normal to the curve (drawn inwards) through the body." This statement is of course incorrect, and is probably intended to refer to motion in a circle. Again, on pages 4 and 5: "It is well known to architects that the lower stones of buildings become compressed by the weight which they support; this is called *settling*." "Settling," as Dr. Jude should know, is due to the displacement, by "compression," or otherwise, of the ground beneath the buildings. On page 26 we are informed that: "On some railways, too, where the rolling-stock is exceptionally good, billiard saloons have been fitted up, and it is possible to play as the train goes along just as if the billiard-table were at rest." It is unfortunate that we are not informed on which railways these saloons are to be found, nor are we favoured with the opinions of the players as to the way the tables "play."

On page 115: "We have, then, the following theorem: *The vertical pressure of a liquid on any immersed surface, of whatever shape, is equal to the weight of the actual column of liquid lying directly above it.*" And this follows a proof on page 113 to the contrary!

Instances of loose and inaccurate statements could be multiplied, but enough have been quoted to show that the sections on "Mechanics" and "Hydrostatics," at any rate, require to be very carefully edited before the next edition is published. The next section, "Pneumatics," contains a good description of the formation of cyclonic and anti-cyclonic areas, and should enable anyone to understand the daily weather-charts published by the Meteorological Office, and to forecast, with a fair measure of success, the probable "weather" in their own locality for twenty-four hours ahead.

The explanation of the supporting action of the aeroplane, on page 176, is not very convincing; Dr. Jude

ignores the influence of the upward slant of the plane altogether; and his reference to a train crossing a rotten bridge in one of Bret Harte's tales is not very apt; for the train could not cross a continuous succession of rotten bridges in the manner indicated.

It is the next section on "Heat," however, on which the book should really be judged, extending as it does over more than 60 per cent of the text; and here it is apparent that Dr. Jude is in his element; for, although there are many indications of hurried writing, we meet with no more of those statements which mar the earlier sections of the book.

Dr. Jude explains the phenomena of heat as manifestations of the internal kinetic energy of the molecules whereof matter is composed, and thence shows the intimate relation between heat and work. In our opinion, he goes too far in this direction, as he constantly refers to so many foot-pounds of heat. Many workers have determined experimentally the ratio between heat units and external work (known as Joule's equivalent); the latest determination by Rowland is (on the British scale), $J=780$. The greater part of this section is devoted to the behaviour of gases under varying conditions of pressure and temperature, whereby the difference between adiabatic and isothermal expansion is explained, and by a natural sequence the theory of entropy is developed. This is from its nature a very difficult subject, and is, moreover, one which is very little known. It is, as Dr. Jude remarks, almost impossible to define it, and it is not, like mass, or time, self-evident as to existence, and only needing precise standards of measurement to make it scientifically definite; but he has succeeded in describing it, in showing how to measure it, and indicated the use of it. On page 619 is described an interesting experiment, whereby a substance can be caused to pass from the state of an ordinary gas to that of an ordinary liquid, or vice versa, without the transition being perceptible at any stage of the process.

The section ends with a history of the kinetic theory of gases; the various modifications adopted from time to time are mentioned, and the numerical results arrived at with regard to the probable mean size and velocity of molecules. No treatment of this branch of physics can be satisfactory without an extensive use of the calculus and higher mathematics generally. Dr. Jude has, however, done very well under his self-imposed limitation.

The final section on acoustics calls for no remarks; it covers the usual ground in the usual manner.

There are numerous examples interspersed through the book, illustrating every theory treated of.

The figures number nearly 400, most of which, except Fig. 3, which ought never to have been admitted, are clear and well-chosen.

There is no index, but one is scarcely needed by reason of the exceptionally full table of contents.

When the blemishes mentioned above are removed, we think there will be a good future before the book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 3, July 16, 1900.

Radio-activity of Uranium.—Henri Becquerel.—The author employed M. Debierne's method to try and extract the radio-active material from uranium. This method consists in mixing uranium chloride with barium chloride, and then precipitating the barium as sulphate. This latter salt carries down with it a very active product, whilst the uranium salt remaining in solution is less

active than it was before this operation. If this operation is repeated a great number of times, the active property of the uranium appears to be gradually extruded, but after about the eighth operation the activity of the uranium diminishes very little. Taking the conductivity communicated to air by the original material as unity, the uranium salt after twelve operations is about half, whilst the activity after eighteen operations is reduced again about one-sixth.

Preparation and Properties of two Borides of Silicon, SiB_3 and SiB_5 .—Henri Moissan and Alfred Stock.—Boron and silicon combine directly at a high temperature, producing two crystalline borides of formulae SiB_3 and SiB_5 . These two new compounds are soluble in melted silicon, from which they may be separated by treatment with hydrofluoric and nitric acids. The crystals easily scratch ruby. They resist the action of most reagents, but the boride SiB_3 is more easily attacked by potash; whilst the compound SiB_5 , richer in boron, is more easily decomposed by concentrated nitric acid. It is curious to compare this simultaneous formation of the two silicon borides, SiB_3 and SiB_5 , with that of the two carbon borides, which are formed in a somewhat similar manner by the action of boron on carbon.

Crystallisation of Gold.—A. Ditte.—If such a metal as gold is placed in contact with the vapours evolved when SO_3 and NaCl react on one another according to the equation $8\text{SO}_3\text{ gas} + 12\text{NaCl} = 6\text{SO}_4\text{Na}_2 + \text{S}_2\text{Cl}_2\text{ gas} + 10\text{Cl} + 68.7\text{ cal.}$, in a porcelain crucible, the whole is heated sufficiently to melt the contained mass of salt and sodium pyrosulphate; the gold is found in a crystalline form, and this at a lower temperature than the fusing-point of the metal. Platinum is attacked in the same way as gold.

Electrolytic Estimation of Bismuth.—Dmitry Balachowsky.—Up to the present time it has not been possible to obtain, by electrolysis salts of bismuth, a sufficiently adherent deposit to allow of washing and weighing. The author has, however, now obtained a deposit of metallic bismuth adhering to the cathode and allowing of washing and quantitative determination. The conditions necessary to obtain this result are—(1) Slight acidity of the solution; (2) absence of large quantities of Cl , Br , I ; (3) not too strong a current (maximum 0.060 ampère); (4) unpolished electrodes. The author's experiments were carried out on sulphate and nitrate of bismuth, but not on the chloride.

Amalgams of Sodium and Potassium.—MM. Guntz and Féréé.—When sodium is dissolved in mercury and the mercury slowly cooled, beautiful crystals of the amalgam separate out. These are of the cubic form, and correspond to the formula NaHg_6 . If, instead of extracting the crystals from the mercury the mass is compressed in leather by hand, still the same amalgam remains; the liquid part, which is filtered off, is mercury saturated with sodium at the temperature of the experiment. The authors attribute this result to the fact of the compound NaHg_6 being a mixture of two amalgams, Hg_6Na and Hg_3Na . The latter amalgam has been obtained in a pure state. They have shown the existence of four distinct amalgams— Hg_6Na , Hg_3Na , Hg_4Na , Hg_5Na . Potassium gives results which are not quite so defined.

Action of Cyanacetic Ethers containing Substituted Acid Radicles on Diazobenzene Chloride and Tetrazodiphenyl Chloride.—G. Favrel.—In a former paper the author showed that the cyanacetic ethers, when reacting on the bis-diazoic chlorides, furnish compounds to which he has provisionally given the formulae which represent the bodies as hydrazones. He now investigates the behaviour of cyanacetic ethers with regard to acid radicles relative to the diazoic and bis-diazoic chlorides. The experiments have been tried with the following ethers:—Ethyl acetylcyanacetate, ethyl propionylcyanacetate, ethyl isobutyrylcyanacetate, ethyl isovalerylcyanacetate, and ethyl benzoylcyanacetate.

CIVIL SERVICE COMMISSION.

FORTHCOMING EXAMINATION.

JUNIOR ASSISTANT in the Department of the WAR OFFICE CHEMIST at Woolwich (20–25), 30th August.

The date specified is the latest at which applications can be received. They must be made on forms to be obtained, with particulars, from the SECRETARY, Civil Service Commission, London, S.W.

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PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN that

ADEMOR NAPOLEON PETIT, of 141, New Street, Newark, in the County of Essex and State of New Jersey, United States of America, has applied for leave to amend the Specification of Letters Patent No. 22867 of 1899 for "Improvements in the Method of and Solvent Materials for Treating Surfaces of Celluloid."

Particulars of the proposed Amendment were set forth in the "Illustrated Official Journal" (Patents) issued on the 9th of August, 1900.

Any person, or persons, may give notice of opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

(Signed),

C. N. DALTON,
Comptroller-General.

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NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 21st. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, 19th September.

THE CHEMICAL NEWS.

VOL. LXXXII., No. 2126.

ARTIFICIALLY RADIO-ACTIVE BARIUM.

By A. DEBIERNE.

M. AND M^{ME}. CURIE have shown that bodies which remain for some time in contact with radio-active bodies become themselves radio-active, owing to the phenomenon of induction. I have tried to obtain induced radio-activity by means of actinium, and I have especially examined its action on the barium salts.

Bodies rendered active by contact with a radio-active body become very slightly active, and the excited mass is also very small. A stronger induced radio-activity and a greater excited mass can be obtained by a more intimate contact, such as obtaining the active body in solution with the inactive substance, or precipitating the two together.

By this means I have obtained an active barium chloride, by allowing the barium to remain in solution with a very active actinium salt.

Still more intense results can be obtained by precipitating barium sulphate in a solution containing actinium. I have already noticed that, under these conditions, actinium is carried down with the barium sulphate on precipitation. The precipitate is now obtained in the form of chloride, from which the actinium can be separated by precipitation by ammonia in the form of hydrate.

If barium and actinium are left for a short time in contact, the induced activity in the barium is insignificant; if left for a longer time, it is found that the induced activity increases with the time of contact, at least for ten days or so. I thus obtained a considerable quantity of radio-active barium chloride, of activity several hundred times that of ordinary uranium. It was very interesting to discover whether the properties of this artificially radio-active barium are the same as those of radiferous barium extracted from pitchblende.

Certain properties are common to both. The radio-activity of barium rendered active by contact is an atomic property in the same way as that of radiferous barium, since it persists in all chemical transformations.

The rays emitted seem to be similar; they ionise gases, provoke phosphorescence of barium platino-cyanide, and act on photographic plates. Further, a portion of the rays are deviated in the magnetic field, and the anhydrous chloride is spontaneously luminous.

Finally, artificially radio-active barium can be fractionated in the same way as the radiferous chloride. When crystallised from water or hydrochloric solution, the chloride which crystallises is more active than that which remains in solution.

This property, which indicates a difference in solubility between the active and ordinary barium chloride, allows of the concentration of the activity, enabling the preparation of products a thousand times more active than ordinary uranium.

However artificially radio-active barium differs from the barium direct from pitchblende, in the following important properties:—It does not possess the spectrum of radium; M. Demarçay examined a product about a thousand times more active than uranium, and was not able to discover the radium lines, whilst with a product only ten times as active as uranium, extracted from pitchblende, the radium spectrum is decidedly visible.

Another important difference has also been observed. The radio-activity of artificially radio-active barium chloride diminishes with time. In three weeks it has diminished to one-third, whilst the activity of radiferous

barium chloride or salts containing actinium begin by increasing, then remain constant. It is very important to prove that this induced radio-activity is not due to traces of actinium or radium. This explanation is scarcely reasonable, considering the methods of separation used. The absence of a spectrum and the diminution of the activity show that this induced activity is due neither to radium nor to actinium.

It is clear, from the preceding, that I have obtained by induction a radio-active barium, which is clearly distinguished from barium and radium, and which apparently is intermediate between these two elements.—*Comptes Rendus*, cxxxi., No. 5, July 30, 1900.

ON THE THEORY OF THE FORMATION OF SULPHURIC ACID.

By E. LOEW.

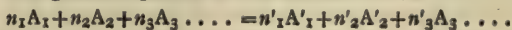
THE contents of each chamber in a sulphuric acid plant consist of a gaseous mixture tending towards a state of equilibrium, but, though this equilibrium is never reached, a stable character is, however, produced, characterised for each chamber by the mean conditions of the composition of the gases and the temperature.

To begin with, the manufacture of sulphuric acid is intermittent. When the gas from the pyrites oven fills a certain space at the ordinary temperature, and steam with the oxides of nitrogen are allowed to mix with it, the reaction will be as follows:—The temperature rises to a maximum, then falls to its original point, the proportion of SO₂ present diminishes and disappears. Liquid sulphuric acid is formed, but not with the speed corresponding to the equation SO₂ + O + Aq = H₂SO₄Aq, as the fumes of sulphuric acid only condense slowly. The process of the reaction is uniform throughout the chamber, but the speed of the reaction is very different at the commencement and the finish, as it is a function of the temperature and the concentration of the reacting gases: when the reaction is complete, the chamber is filled with a homogeneous gaseous mixture, though during its progress—owing to inequalities of temperature, &c., at different points—the gaseous mixture may not always be absolutely homogeneous.

The most convenient chamber for the study of the theory of the formation of sulphuric acid would be one constantly filled with a homogeneous gaseous mixture, in which the gas was admitted, and passed out not at one point only, but at an infinite number of points, uniformly throughout the chamber: such a chamber, however, cannot exist.

The law of Guldberg and Waage can, however, be applied to any fraction of a chamber, and the mean gaseous composition calculated therefrom. Admitting that the reaction of the homogeneous mixture takes place at a constant temperature, the law of masses is applicable.

The general equation of the reaction is:—



where A represents the kind, and *n* the number of molecules. Let *c*₁ *c*₂ *c*₃ ... be the number of grm.-molecules of the substances A₁ A₂ A₃ ... per litre, then the speed *V* of the reaction is:—

$$V = v - v' = Kc_1c_2c_3 \dots - K'c'_1c'_2c'_3 \dots$$

(*K* and *K'* being constants of proportion),—that is to say, the speed of the reaction produced in the direction of the equation (from left to right) is proportional to the production of the active matter. The compounds reacting are SO₂, H₂O, O₂, N₂O₃(NO). If the reaction leads to nitrosyl sulphuric acid, it may very well be reciprocal. Manufacturers agree that between 50–60° is the best temperature, at which the decomposition of the nitrosyl sulphuric acid is still slight, but, on the other hand, when the temper-

ature rises, $v' = K c_1' c_2' c_3' \dots$ acquires a value nearer to $v = K c_1 c_2 c_3 \dots$, and finally $v' = v$,—that is to say, that the system is in equilibrium, and no more sulphuric acid is formed. These suppositions, however, have yet to be proved. Experiments have shown that the relations of concentration are a measure of the speed of the reaction; it remains to be seen whether it is really according to the formula—

$$V = v - v' = K c_1 c_2 c_3 \dots - K c_1' c_2' c_3' \dots$$

This has not yet been confirmed.

An excessively energetic reaction has been observed in the first part of the chamber, and a stoppage of the reaction in the second part. I propose to show that this observation is erroneous, and that the second part of the chamber also takes part in the reaction, according to the composition of the gases it contains.

Lunge's conclusions, drawn from the proportion of SO_2 present, can be equally well deduced from the oxygen.

A glance at the analyses reveals figures which may be explained, but which cannot logically be used for explaining the course of the reaction. According to the proportion of SO_2 , Lunge calculates for different parts of the chambers, the progress of the reaction as follows:—

Where the sample for analysis was taken from.	First chamber, beginning.	First chamber, middle.	Junction of first and second chambers.	Second chamber, middle.	Junction of second and third chambers.	Third chamber, exit.
Calculated by Lunge and Naef	57.7	78.15	80.1			
Calculated from the proportion of O_2	54.1	72	80.9			
Lunge and Naef	—	74.8	77.47	94.52	95.45	99.6
Calculated from the O_2	—	67	72	90.6	95.5	100
Lunge and Naef	48.63	59.23	73.9	96.84	97.13	99.3
Calculated from the O_2	65.4	73.7	84.2	100	100	100

It is necessary to find an explanation why the reactions almost entirely cease in the second part of the chamber, and then re-commence energetically in the next chamber. The gases arrive from the furnace full of activity, and both chemical and mechanical reactions take place with energy. It is this violent mixture of the gases which makes a system composed of a single chamber irrational, as it is impossible to maintain a high concentration if the escaping gas is to be free from SO_2 . The greater the quantity of gases in the chambers, compared with the amount of gas coming from the furnace per unit of time, the more equal will their composition keep; also, the more energetic the movement of the gases, and the more the differences produced by the chemical reactions become equalised, the more uniform will the composition of the system be. It remains to be proved experimentally whether the gases become mixed throughout the chamber, and whether the reaction follows the concentration of the gases, as different authors do not agree on this point.

If we suddenly add nitric acid to the contents of the lead chamber, the temperature instantly rises in the first part of the chamber, but in a few minutes the rise is noticed at the further end. In a few more minutes the nitric acid commences to act at the further end. According to different methods of manufacture, the gas takes from two to four hours to traverse the system. The actual direction and speed of the gas is of no importance. In a system of chambers receiving a sudden excess of 4 kilos. of nitric acid through the Glover tower, the following observations were made:—

	At 6 metres from the first side we observed—	At 30 metres from the first side we observed—
	°C.	°C.
Normal progress	56	53
On addition of HNO_3	56.0	53.0
After 2 minutes	57.0	54.0
" 5 "	60.0	56.0
" 6 "	61.0	58.0
" 9 "	61.5	59.0
" 10 "	62.0	60.0
" 15 "	64.0	61.0
" 20 "	65.0	60.5
" 25 "	66.0	59.5

This can only be explained by admitting that a part of the gases from the furnace had a speed considerably above the mean,—that is to say, that the gases were mixed throughout the chamber. The gases mix with difficulty; but when they reach a part of the chamber where the temperature is distinctly different and chemical reactions take place, and an external cooling causes the formation of currents, the conditions for mixing are apparent.

The chemical reactions which take place in the lead chambers are governed by the temperature and the concentration of the reacting molecules. Each part of the chamber has an effect proportional to its concentration. We will now consider the relations of these concentrations.

1. *Steam*.—The maximum quantity of steam which can exist in a lead chamber depends on the vapour-tension of the sulphuric acid formed at the local temperature. If the temperature be 50° , and the strength of the acid 5°B , the vapour-tension is 10.9 m.m. according to Sorrel, and the density—

$$d = \frac{5}{8} \times \frac{0.00129}{1 + 0.003665 t} \times \frac{p}{760} = 0.00001.$$

One cubic metre of gas contains 10 grms. of steam. To form 153 grms. of acid at 51°B , 73 grms. H_2O and 64 grms. SO_2 are required. The chamber thus contains the amount of water equivalent to 8.77 grms. SO_2 per cubic metre,—that is, 3.05 litres at 0° , or 3.6 litres at the temperature of the chamber. If we keep the acid at 49.7°B , and the temperature at 60° , the corresponding quantity of water is equal to 17.2 grms. SO_2 per cubic metre, or 0.73 vol. per cent. Chambers which contain too much sulphurous acid are always deficient in water. The necessary amount of steam can only be introduced at one point, but, as the vapours mix rapidly, this condition is favourable, but we must not be too sure that this is the best. It is necessary to introduce water by as many orifices as possible in chambers where the proportion of SO_2 is high; we should therefore expect to get an acid of much greater dilution.

2. *Oxides of Nitrogen*.—The addition of oxides of nitrogen may be increased to a certain extent, but it is practical considerations only which fix the limit. The high production of French chambers necessitates a high consumption of nitric acid. It is not possible to increase the production of a chamber by increasing the proportion of any of the other bodies which enter into the reaction. It should be taken as proved that it is not the relation of the concentrations that determines the speed of the reaction. The chambers use more SO_2 in winter than in summer, and for a plant of 3000 cubic metres (3 chambers) this increase reaches 15 per cent; the consumption of oxides of nitrogen, calculated to nitric acid at 36°B , is from 0.9 to 1.1 per cent in summer, and from 0.93 to 1.2 per cent in winter, of the quantity of sulphuric acid at 60°B obtained. The temperature of the first two chambers is practically the same in summer and winter. We can therefore only attribute this increased production in winter to the greater cooling of the sides and the better condensation of the sulphuric acid fumes. There is no reason to doubt that the reaction takes place as described by Lunge. If the oxides of nitrogen become fixed in the state of nitrosyl sulphuric acid, the proportion of gas in

one of the reacting bodies diminishes, and the reactions which tend to destroy the compound formed ought therefore to play a part in the formation of the sulphuric acid. The speculations of Sorrel on the vapour tension of nitric acid in the presence of sulphuric acid throw a great deal of light on these phenomena.

3. *Oxygen*.—The proportion of oxygen varies within certain limits, according to the amount of SO_2 in the gas from the pyrites furnace.

4. *Sulphurous Acid*.—From what we have said above, the higher limit of the proportion of sulphurous acid can be determined. The relation between the proportions of O_2 and SO_2 is not to be neglected, according to the Guldberg-Waage law; it can be calculated whether it is more advantageous, for example, to work with the furnace giving a gas richer in oxygen and poorer in sulphurous acid, or the contrary. As a general rule, the average proportion in SO_2 of the chamber-gases is lower than that of the furnace-gases. We determine the mean proportion to be kept up in each chamber, knowing that this chamber ought to supply the next with a given quantity of gas of such proportions that the following chambers can complete the reaction. It is evident, therefore, that a plant consisting of a single chamber will give a very poor return.

We must consider a definite concentration of SO_2 , N_x , O_y , H_2O , and O , for certain conditions, as the normal concentration; a variation from this standard leads to an abnormal condition, and it must be remembered that, under certain circumstances, the contents of the first chamber of a system may undergo rapid variations, which, however, are of short duration, and are hardly felt in the following chambers; once the normal conditions are re-established in the first chamber, the proper concentrations remain a long while in the second. The analyses of the gases may sometimes lead to confusion; the second chamber may show over production while analysis shows the contrary; we find, for example, x per cent of SO_2 entering and y per cent leaving, while actually the chamber may have consumed a larger proportion of SO_2 than has entered, and has only lost a part of the abnormal quantity it contained; this, however, is an extreme case.

To sum up it may be said:—

1. The chemical reactions giving rise to the formation of sulphuric acid follow the Guldberg-Waage law, each part of the chamber giving a production corresponding to its concentration in reacting matter.

2. The mixture of the gases is complete, and the composition of the contents of the two halves of the chamber practically identical.

3. The proportion of O_2 to SO_2 is constant; it varies within certain limits according to the size of the chamber.

4. By adding an excess of oxides of nitrogen, and by creating conditions by which a greater proportion of steam can be kept up, the speed of the reaction in the chambers can be increased.

5. The difference in temperature of two chambers is in strict relation with the manner in which the reaction $\text{SO}_2 + \text{O} = \text{SO}_3$ is divided between them.—*Zeitschrift für Angewandte Chemie*, April 3, 1900.

Combination of Sulphate of Nickel with Hydroxylamine.—R. Uhlenbuth.—When we add anhydrous hydroxylamine to a cold saturated solution of SO_4Ni , the green colour of this salt gives place to an azure blue, and finally to a deep red tint. The solution then slowly (or rapidly on the addition of a little alcohol) deposits red crystals, probably quadratic, of the salt $\text{SO}_4\text{Ni} + 6\text{NH}_2\text{OH}$ (instead of $6\text{H}_2\text{O}$), which consists of the hydrated crystals. These crystals are decomposed by water and by alcohol, with the separation of a white powder which has not yet been examined. On heating the red salt it swells up and changes colour, becoming successively blue and then green. The blue salt, without doubt, contains less hydroxylamine.—*Lieb. Ann. Ch.*, vol. cccvii., p. 332.

THE GASOMETRIC MEASUREMENT OF NITRITES IN THE PRESENCE OF NITRATES OR OTHER SOLUBLE SALTS.

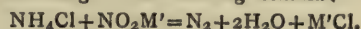
By J. GAILHAT.

HAVING had occasion to estimate the proportion of nitrites contained in various saline mixtures during a research on the nitroprussiates, we were led to the conclusion that among the various methods recommended for this purpose but few possess the precise and practical qualities necessary for obtaining good results.

The use of the manganimetric method, not to mention others, is very much restrained by reason of a large number of substances, as many mineral as organic, which act on the permanganate under the conditions of the experiment.

The following process has the advantage of being available under widely different conditions, while all the time retaining its absolute exactitude.

When, to an excess of a neutral, boiling, concentrated solution of sal-ammoniac, we add a solution of a metallic nitrite also neutral, we get a regular disengagement of nitrogen according to the following formula:—



The equation shows us that to get at the quantity of nitrite engaged in the reaction, it suffices to determine either the amount of sal-ammoniac decomposed, the nitrogen given off, or the fixed chloride produced. Practically, however, the nitrogen gas is the most readily adapted to a simple and rapid experimental estimation; it can easily be collected and accurately measured.

The apparatus we have made use of is the same as that used by M. Schloesing for the gasometric estimation of the nitrates. We have adapted to it an escape tube formed in a single piece, and fitted with a tap which greatly facilitates the operation. Further, the water-jacket is deep enough to allow of the complete immersion of the tubes graduated to tenths of a c.c. in which the nitrogen gas is collected. Finally, we constantly maintain a current of water through this jacket sufficient to prevent any rise of temperature.

Thanks to these precautions, the cooling of the water contained in the tubes being assured, the gases held in solution are unable to come off, and the nitrogen collected is also unable to be dissolved therein, as this water is already saturated.

To conduct an operation the flask is filled to about two-thirds of its volume with a saturated solution of chloride of ammonium; the apparatus is set up, and the temperature brought to boiling-point, with the taps remaining open. The pressure causes the liquid in the funnel tube to rise, and the tap is turned as soon as the liquid reaches its level. The boiling is allowed to proceed until all the air is driven off. We can make sure of its complete expulsion by closing the tap of the escape tube for a moment; the water in the water-jacket then rises up to this tap, making a sharp little noise. If, at this moment, any gas remained in the tube, the quick opening of this same tap would easily allow it to be driven out on account of the increase of pressure produced in the flask during this little manœuvre, which may be repeated two or three times to make sure of the complete absence of any trace of air. We then place in the funnel 10 c.c. of solution of the nitrite to be estimated, of which the approximate amount present should be between 5 and 10 grms. per litre; the graduated tube is placed at the end of the escape tube, and kept slightly inclined at the bottom of the water-jacket; the nitrous solution is then allowed to run in, taking the necessary precautions for preventing any absorption. The rapid, regular disengagement of gas soon commences; the funnel is rinsed two or three times, and the nitrogen allowed to come off completely. This can be verified as shown above.

All the readings are made at the same moment, noting the temperature, the barometric pressure, and the vapour tension of the water under these conditions. Thus we have all the elements for the calculation. The vapour X, the weight of nitrite contained in a litre of the solution under examination, being given by the expression:—

$$X = \frac{100 M}{14} \times \frac{V}{2000} \times \frac{H-f}{(1+a f) \times 760} \times 0.9712 \times 1.293,$$

in which M represents the molecular weight, or rather the equivalent of the nitrite estimated, and V the volume of nitrogen obtained expressed in cubic centimetres, the half of which only comes from the nitrite, the remainder being due to the decomposed sal-ammoniac.

We have checked the accuracy of this method by means of solutions of nitrite of potassium purified with alcohol, taking varying quantities, then weighing rapidly after fusing the pure salt and cooling in an exsiccator, as well as by estimations made by the manganimetric method with solutions of nitrite of potassium and nitrite of sodium.

	I.	II.	III.	IV.
Expt. made with 10 c.c. of a solution of—	NO ₂ K	NO ₂ K	NO ₂ Na	NO ₂ Na
Containing per litre, G.ms.	9.81	5.94	—	—
Value of V, C.c. ..	1. 26.72	18.48	20.75	26.20
	2. 26.70	18.52	20.80	26.25
	3. 26.80	18.50	20.82	26.25
	4. 26.75	18.54	20.80	26.28
	5. 26.73	—	—	26.23
Corresponding value of X,				
G.ms.	9.84	5.97	5.32	7.57
Result given by the	1. 9.74	5.80	5.28	7.58
MnO ₄ K method. {	2. 9.78	5.86	5.31	7.64

The agreement is perfect; the process may be used, in most cases, where the salt to be estimated is in the form of a more or less complex mixture.

We can also operate comparatively, in a more simple manner, with a typical solution of nitrite obtained from a pure salt, and weighed or titrated colorimetrically.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xii., No. 1.

REFRACTIVE INDEX AND ALCOHOL-SOLVENT POWER OF A NUMBER OF CLEARING AND MOUNTING MEDIA.*

By C. E. M'CLUNG.

As far as the author's observation goes, there has not been published any very extensive list of the refractive index and clearing value of the reagents commonly used by microscopists. Such a want is noted by Lee in the fourth edition of his "Vade Mecum," page 66. In the hope of assisting in the compilation of such valuable information, the writer has experimented on the reagents named in the following table, with the results there noted. The instrument employed in the determination of the refractive index was the Pulfrich refractometer, the sodium flame being used as the source of illumination and the conditions of temperature being kept as nearly constant as possible.

In ascertaining the clearing value of the substances, a number of methods were tried, but finally abandoned for the simple one of testing the strength of alcohol that would dissolve in the reagent and produce a clear solution. While this method does not truly represent the conditions present in a tissue where the clearing agent is replacing the absorbed alcohol, yet actual practice indicates that the results are approximately correct, at least nearly enough so to make the figures of practical value. Strengths of alcohol varying by 5 per cent were employed, and the weakest one that the reagent would dissolve is given in the table as the lowest grade of alcohol from which it will clear.

The different substances tested were taken from the ordinary laboratory supply, and supplemented by others obtained from the Pharmacy department of the University. The latter consisted almost entirely of essential oils from the house of Lehn and Fink, New York. When possible, more than one sample of each reagent was obtained and tested.

Following is the table:—

	Refractive index.	Strength of alcohol dissolved. Per cent.	Price per pound. Dollars.
Chloroform	1.4395	95	0.65
Linalool	1.45941	80	—
Oil, Eucalyptus ..	1.46090	90	1.25
Linaloe	1.46090	85	—
Oil, Petitgrains ..	1.46090	90	—
" Coriander	1.46288	85	0.75 oz.
" Peppermint	1.46327	85	1.25
" Cedar	1.46626	95	0.30
" Pinus sylvestris ..	1.46882	100	1.10
Turpentine	1.46882	100	1.40 gal.
Oil, Lemon	1.47078	95	1.25
" Eucalyptus glob.	1.47097	90	—
" Orange	1.47176	95	4.00
" Pinus picea	1.47274	100	—
" Juniper berries ..	1.47394	95	1.75
" Pinus pimlionis ..	1.47620	100	—
" Citronella	1.47909	90	1.25
" Origanum	1.47919	95	1.10
Turpeneol	1.48005	75	—
Oil, Celery	1.48054	95	1.20
" Nutmeg	1.48054	95	0.30 oz.
" Origanum	1.48103	95	1.10
" Caraway	1.48441	90	1.75
" Ginger	1.48807	95	0.65 oz.
Xylene	1.49348	95	—
Benzene	1.49488	95	0.45
Carvol	1.49535	85	—
Oil, Thyme	1.49638	95	1.49
" Copaiva	1.49723	Immisc.	1.10
" Cedarwood	1.50188	95	—
"	1.50326	95	—
" Cumin	1.50373	90	4.50
" Sandalwood (E. In.)	1.50510	90	6.00
" Calamus	1.50602	95	0.30 oz.
" Sandalwood (W. In.)	1.50820	80	3.50
" Cedarwood	1.51533	95	—
Xylene balsam ..	1.52397	—	—
Oil, Sassafras	1.52724	95	0.50
" Allspice	1.53062	85	0.25 oz.
" Cloves	1.53171	80	0.65
" Sweet birch	1.53329	90	—
" Cinnamon leaves ..	1.53535	85	—
Safrol (sp. gr. 1.108) ..	1.53584	95	—
Oil, Fennel	1.53885	95	1.75
" Cloves	1.53723	80	0.65
" Mirbane	1.54982	95	0.35
" Anise	1.55795	95	2.25
Anethol	1.55208	90	—
Anilin	1.58457	60	—
Oil, Cassia	1.60160	80	1.80

The table speaks for itself, so that comment is scarcely necessary. From the list given, a series of clearing agents may be selected in which almost any refractive index from 1.44 up to 1.60 is obtainable. Since many of these are suitable agents in which to mount objects, the proper refractive power for most structures may be selected. Where it could be found, the price of the reagent per pound is given.

Particular attention is called to the value of the oil of cassia, which has a refractive index of 1.60160 and clears from 80 per cent alcohol. It is a most excellent reagent according to all experience in the laboratory, and in addition to its other good qualities, it dries hard enough to make permanent mounts.

* From the *Kan. Univ. Quarterly*, vii., No. 4.

SYNTHETIC INDIGO.*

By EDWARD S. JOHNSON.

IT is a matter of very general observation that in this centre of occidental civilisation, the United States, the reception accorded scientific discovery by the mass of intelligent men is notably apathetic unless prospect for immediate utilisation is evident. This fact is pointed to as a marked characteristic of the American by the enlightened nations of the Old World, where, pre-eminently in Germany, the greatest importance is attached to scientific research and discovery whatever the momentary outcome.

The causes of these divergent social conditions cannot consistently be made here a subject of minute discussion. It suffices to refer to the influence of environment and other factors of natural selection in their bearing upon the older civilised nations treated purely as modified varieties or races of the *genus homo*, and the intensity, not to say fierceness, of the struggle for existence occasioned by the narrow limits naturally prescribed for a multitude of combatants. Such conditions have resulted in resort to all the refinements of human intelligence to maintain a successful struggle; in all branches of industrial affairs, aid has been drawn from institutions of learning with such apparent advantageous effect as to establish in those countries where scientific light is brightest an intimate connection with, and supreme respect for, science in its purity and the increasing host of its devotees.

Cultured young America has not been altogether backward in an appreciation of such matters in what has been his absorbing occupation, the amassing of wealth. The untold natural resources of a new land he has in part brought to light, utilised to his own comfort and set his sons of the last decades of the century upon a career of development unparalleled in rapidity and immensity to a degree which makes America an object of utter amazement to the more cultured of older civilisations. With this growth has come a severity of competition in all those forms of great organised effort of civilised man, known in part in social economics as industry and commerce. Natural science is exerting in all departments of industry an elevating influence. The united efforts of botanist, zoologist, and chemist are fast placing agriculture upon a rational footing, and those manufacturing industries producing the great staples which serve as raw materials for the almost innumerable objects of cultured necessity and comfort are directed each year more fully than ever by the deductions of physical and chemical science.

Many stages of progress must, however, still be attained and passed before American industry may generally be regarded as upon the level of that of the leading nations of continental Europe in respect to an appreciation and application of scientific methods and observations. That period of development has hardly passed in which a proffered advantage is eagerly accepted, fairly grasped by the beneficiary, while the benefactor is relegated to forgetfulness, or, if remembered, referred to with a kindly commiserative, amused smile, when engaged upon problems of science not promising an instant contribution to material wealth. Leaving the figure of the youth in the first years of robust manhood, with fine muscular development and general functions, but with an indefinite sense of the source of his well-being, American industrial conditions may be again likened, in a measure at least, to those of the newly discovered gold-fields. Methods of operating are adapted to a dazzling natural wealth of raw material to be converted into finished product by a mere turn of the hand, for the very picking up, or, at most, the crudest forms of placer mining. The mass of fabulous treasure contained beneath the surface in great alluvial deposits and beds of quartz rock is neglected for the time, and left for

the systematic and refined operations of the metallurgist, who in after years applies the knowledge of his science with the utmost economy in the transformation of his raw materials. This latter period of the gold field's history illustrates in main features European industrial conditions.

Nothing offers a more forceful illustration of the important part which the cultivation of science, for its own sake, has played in their development to the present exalted level than the following, at first glance apparently insignificant incident, from the history of synthetic indigo.

In pursuance of confirmation of his theory of the relationship of indol to the compounds of the indigo-group, Baeyer (*Ber. d. Deutsch. Chem. Ges.*, xiii., 2254; *Ueber d. Beziehungen d. Zimmtsäure zu d. Indigogruppe*) sought evidence in the reduction of isatine to diosindol, oxindol, and finally indol. Success was ultimately achieved, but not without the expenditure of, seemingly, a wasteful amount of time and energy to discover the right reducing agent. This was found in the now classic, although common, zinc-dust of the laboratories, which has been, and is, of greatest service to the practice of chemical research, and literally has led to the establishment of a gigantic chemical industry. It was by the application of the new reducing agent that Graebe and Liebermann, respectively assistant and pupil in Baeyer's laboratory, in 1868, discovered the constitutional relation of alizarine to anthraquinone and anthracene, and soon were led to invent means for a synthesis of the celebrated colouring-matter which, authentic accounts relate, produced the flaming reds of the Far East centuries and centuries ago.

The cultivation of the madder plant, the source of this ancient dye-stuff, gradually kept westward, and it is related (Schultz, *Chem. d. Steinkohlentheers*, ii., 584) that, as early as the seventh century, the plant was grown on a small scale in France, which became, however, several centuries later, with favourable climatic conditions, the most extensive European producer of madder, the ground root of the colour-bearing plant. Besides France, Holland engaged notably in the cultivation. In the season of 1862-3, the production (Schultz, *Chem. d. Steinkohlentheers*, ii., 597) of madder in France had attained the seemingly proportions of 26,850 tons; ten years later, 1871-2, and two years after the introduction of artificial alizarine, 25,000 tons were still harvested; in 1878-9 this sum had decreased, gradually at first, and then by leaps and bounds, to 500 tons. A similar, but less rapid, fate overtook the production in other madder-growing lands, dwindling the estimated total output of the root, 70,000 tons, for the years about 1868 to a mere trifle. The rapid decline in the cultivation was accompanied, which was still more disastrous to the madder-grower, by a fall of 75 per cent in price. This is concretely exhibited by the fact that in 1860 the value of madder and garancine exported by France was nearly 6,250,000 dols., an amount which had decreased, for the same items in 1876, to somewhat more than 900,000 dols.

By these industrial changes, no mean crisis had presented itself. Vast tracts of valuable agricultural land must be turned to lucrative account, and extensive commercial organisations must be dissolved or seek excuse for existence in other fields. While a temporary disturbance was occasioned, the general effect can only be regarded as beneficent; the development of the great staples of agriculture was elevated where such was urgently needed by the return of former madder-fields to their cultivation. It is most interesting to note the influence of the innovation upon chemical industry, the facts of which relate a familiar story, but one of such cardinal character as to bear frequent recounting, marking, as it does, an epoch in the history of applied chemistry. By the announcing of a practicable manufacture of alizarine from anthracene, the preparation of the latter became one of the most important and lucrative operations of the coal-tar distilleries. For the conversion of anthracene into anthraquinone, a heavy demand was made upon the

* *Proceedings of Engineers' Society of Western Pennsylvania*, xvi., No. 3.

producers of the alkali chromates. In succeeding transformations, the sulphonation and oxidising fusion, fuming sulphuric acid, caustic alkali, and potassium chlorate are required. Their supply by the acid, alkali, and chlorate industries gave each a strong forward impulse, adding heavily to the production.

This splendid industrial expansion, which the enthusiastic chemist cannot regard but with keen pleasure and pride, may be directly referred for its origin to the simple observation of the value of zinc-dust in the study of a group of substances belonging in a totally different field of scientific research from that by which by its means was later illumined and cultivated with marvellous results. The influence of this reagent as an industrial factor did not cease with the founding of the alizarine manufacture. Its part in revealing, in the hands of Baeyer, the relationships of indigo, and leading thus finally, in the course of years and a series of researches of unequalled brilliancy, to practicable methods for its synthesis, marks the distant beginning of another economic change now steadily progressing toward certain successful culmination.

(To be continued).

ON THE EFFECT OF VERY LOW TEMPERATURES ON THE COLOUR OF COMPOUNDS OF BROMINE AND IODINE.

By J. H. KASTLE.

SOME time ago the writer called attention to the fact that the characteristic red, orange, or yellow colour of bromine and iodine compounds could probably be accounted for on the supposition that the halogen compounds exhibiting such colours are slightly dissociated even in the solid state, and that the characteristic colour, therefore, is simply that of the halogen itself. The following facts were cited in support of this conclusion:—

1. The colour intensity of the halogens is in inverse ratio to their chemical activity, and may be represented roughly at least by $F < I$. Similarly, the colour intensity of their compounds by $MF < MI$. Further, the colour of bromine and iodine compounds is altogether similar to that exhibited by certain solutions of these two elements.

2. The perfect continuity exhibited in the colour changes of such easily dissociable substances as phosphorus pentabromide in passing through the solid, liquid, and gaseous states.

3. Those halogen compounds are the most highly coloured which are the least stable, and whose elements are held in combination by the weakest affinities.

4. On heating, the colour of halogen compounds becomes darker and deeper in tint.

It also follows that, if the characteristic colour of bromine and iodine compounds is due to dissociation, the colour of these compounds ought to become lighter in tint, if not altogether white, on cooling to very low temperatures. At the time of my first communication on this subject, no opportunity was afforded for trying the effect of very low temperatures on the colour of the compounds in question. Through the kindness of Dr. Freer, of the University of Michigan, and Dr. Simon, of the College of Physicians and Surgeons, Baltimore, I have recently been able to try the effect of very low temperatures (the boiling-point of liquid air -190°) on the colour of certain of these halogen compounds. On the 9th of March Dr. Freer lectured on liquid air in the city of Louisville, and on the 22nd of March Dr. Simon lectured in Cincinnati on the same subject. At the close of the lecture both of these gentlemen kindly placed at my disposal a quantity of the liquid. The following compounds were selected for experiment:—Lead iodide, phosphorus pentabromide, phosphorus heptabromide, mercuric

iodide,* iodoform, mercuric bromide, benzenedibrom-sulphonamide, and tribromphenol bromide. Small amounts of these compounds in pure condition were placed in sealed tubes. These were then immersed in liquid air in a Dewar tube, and allowed to remain in the liquid until no further alteration of colour was observable. The colour of these compounds before and after cooling in liquid air was observed to be as follows:—

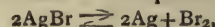
Substance.	Colour at ordinary temperatures.	Colour at the temperature of liquid air.
Lead iodide . . .	Golden yellow..	Pale sulphur-yellow.
Phosphorus pentabromide . . .	Citron yellow ..	White or very pale yellow.
Phosphorus heptabromide (a) . . .	Red	Yellow.
Mercuric bromide . . .	Pale yellow ..	White.
Iodoform . . .	Yellow	White, or nearly so.
Benzene dibrom-sulphonamide..	Orange	Pale sulphur-yellow.

Tribromphenol bromide . . .	Yellow	Very pale yellow.
Mercuric iodide . . .	Red	Orange yellow.

(a) This compound has hitherto been regarded as the red modification of phosphorus pentabromide. Kastle and Beatty have recently shown, however, that the substance is in reality a higher bromide of phosphorus, probably the heptabromide, PBr_7 .

It will be observed that all of these compounds became markedly lighter in colour on cooling to $-190^\circ C.$, and in some cases the change of colour was most striking. It would seem, therefore, that these results tend to confirm the idea that the colour of halogen compounds is due to dissociation.

Before leaving this phase of the subject, it might be well to call attention to an observation by van't Hoff. In his "Etudes de Dynamique Chimique" (Eng. Trans., p. 273) he points out that at $60^\circ C.$, *in vacuo*, silver bromide dissociates in the sense of the equation—



and that silver bromide at 60° *in vacuo* will decompose until the bromine vapour evolved has reached a pressure of 2.9×10^{-5} m.m.

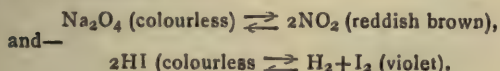
It would seem to be generally, if not universally, true that coloured substances become lighter in colour on cooling to very low temperatures. That such is the case may be seen from the following:—

Substance.	Colour at ordinary temperature.	Colour at -190° .
Bromine . . .	Dark red, opaque	Orange-red.
Iodine, solid . . .	Steel-grey ..	Steel-grey.
Iodine, in alcoholic solution . . .	Brown	Very light yellowish brown.
Iodine, in carbon disulphide solution . . .	Pink	Very light pink.
Sulphur, rhombic.	Sulphur yellow.	Nearly colourless.
Phosphorus, red modification . . .	Dark crimson ..	Ferruginous brown
Copper sulphate..	Dark blue.. ..	Dark blue.
Chrome alum . . .	Dark plum colour	Pinkish violet.
Manganous chloride . . .	Pink	Very light pink.
Chromic chloride.	Violet . . .	Pink.
Phenolphthalein (alcoholic solution, alkaline)..	Pink	Colourless.
p-Nitrophenol (alcoholic solution, alkaline . . .	Yellow	Lighter yellow.

* Other observers have found this compound to become yellow in boiling oxygen.

At the temperature of liquid air fluorescein and eosin in alkaline alcoholic solutions retained their characteristic colours, but became considerably lighter in tint.

From these few observations it would scarcely be logical to conclude that the lightening of colour produced by cooling to very low temperatures is in all cases due to the same cause as that which operates in the case of bromides and iodides. On the other hand, it is an interesting and suggestive fact that any increase in the depth of colour produced by rise of temperature is usually accompanied by a corresponding increase in the chemical activity of the substance, and with such facts before one it is almost impossible to keep out of mind such reversible processes as the following:—



In the light of the electrolytic dissociation theory regarding the action of indicators, the effect of very low temperatures on the colour of an alcoholic solution of phenolphthalein which has been rendered alkaline with caustic soda, is certainly most remarkable and interesting.

There is still another point of interest connected with this subject. This is regarding the effect of very low temperatures on the colour of allotropic modifications of the same substance. It is well known that the red modification of mercuric iodide becomes orange-yellow when cooled in liquid oxygen, and that on removal from the bath of liquid oxygen it quickly changes to red again. By some chemists this has been construed to mean that at very low temperatures the yellow variety of this compound is more stable than at ordinary temperature, and that the yellow form of the iodide obtained by great cooling is identical with that produced by heating above 128° (Newth's "Inorganic Chemistry," 5th edition, p. 558). There can be little doubt regarding the correctness of the first of these conclusions, namely, that the yellow modification of mercuric iodide is more stable at these very low than at ordinary temperatures. It has been shown, for example, that at -35° monoclinic sulphur changes to orthorhombic about five hundred times more slowly than at ordinary temperature (See also "The Phase Rule," Bancroft, 32-34). To conclude, however, that the yellow form of mercuric iodide obtained by cooling the red to -190° C. is identical with the yellow variety obtained by heating the red to 128° is certainly incorrect, as may be seen from the following:—

Small amounts of mercuric iodide were sublimed in test-tubes. These tubes were then allowed to stand until a certain amount of the yellow had changed to red. Both the red and yellow varieties of this compound were thus obtained side by side in the same tube. On placing such tubes in liquid air, it was observed repeatedly that the red variety of the compound became orange-yellow, and that the yellow variety became white or very pale yellow. Above the level of the liquid air the yellow modification of the compound retained its ordinary yellow colour, thereby rendering these differences in colour the more pronounced by contrast. The difference in colour between the red and yellow modifications of mercuric iodide at -190° C. was thus rendered plainly visible. The effect, therefore, of these very low temperatures on the red modification of mercuric iodide is not to convert it into the yellow variety stable above 128°, but simply to lighten its colour in a manner characteristic of other coloured bromides and iodides. Therefore, at all temperatures below 128°, the red and yellow modifications of mercuric iodide are distinctly different substances.

In conclusion, I desire to thank Professors Freer and Simon for their kindness in furnishing the liquid air necessary for these experiments.—*American Chemical Journal*, xxiii., No. 6.

THE ACTION OF AMMONIUM CHLORIDE UPON NATROLITE, SCOLECITE, PREHNITE, AND PECTOLITE.*

By F. W. CLARKE and GEORGE STEIGER.

In our last paper upon the ammonium chloride reaction (*Am. J. Sci.*, Feb., 1900; *CHEM. NEWS*, lxxxi., 187), we showed that analcite and leucite, when heated to 350° with this reagent in a sealed tube, both yielded the same compound, ammonium leucite, $\text{NH}_4\text{AlSi}_2\text{O}_6$. We also showed that the reaction was not limited to these minerals, but that it was fairly general in character, and that with other species analogous results could be obtained. We now have data relative to four more minerals, and these exhibit a range of variation which well illustrates the availability of the method for investigations into the chemical constitution of silicates. Three of the species now studied have previously been regarded by one of us as analogous in structure, provided that all or part of their water can be interpreted as constitutional, and the formulæ assigned were as follows:—

Scolécite	$\text{Al}_2(\text{SiO}_4)_3\text{CaH}_4\cdot\text{H}_2\text{O}$
Natrolite	$\text{Al}_2(\text{SiO}_4)_3\text{Na}_2\text{H}_4$
Prehnite	$\text{Al}_2(\text{SiO}_4)_3\text{Ca}_2\text{H}_2$

Two of these formulæ must now be abandoned, because of the experimental evidence which we have obtained. We may first study the three species individually.

Natrolite.

In our former paper we reported a crude, preliminary experiment made upon impure, yellowish natrolite from Aussig in Bohemia. After heating with ammonium chloride in a sealed tube, and subsequent leaching with water, 17.56 per cent of soda was extracted, and in the residue 8.29 per cent of ammonia was found. Natrolite, therefore, was a suitable mineral for further investigation, and our expectations regarding it have been fully confirmed.

The material available for our new experiments came from the well known locality at Bergen Hill, New Jersey, and consisted of a mass of slender needles densely matted together. Part of the uniform, ground sample was analysed, with fractional determinations of the water, and part was used for the sealed tube experiments, precisely as in the research upon analcite and leucite. Three of these experiments were made, and in each case the natrolite was mixed by grinding in an agate mortar with four times its weight of dry ammonium chloride, after which it was heated to 350° in the sealed tube. Even during the grinding a slight reaction took place, and a distinct smell of ammonia was given off by the mixture. With pectolite the same smell was perceived. The three experiments may be summarised as follows:—

- Heated eleven hours. Upon leaching, 14.89 per cent of soda and 1.20 of lime were extracted. In the residue 9.26 per cent of ammonia was found.
- Heated nine hours. Leach not examined, 9.26 of ammonia in residue. The complete analysis of the residue is given further on.
- Heated three hours. 14.09 per cent of soda and 0.20 of lime were extracted. The residue contained 8.87 per cent of ammonia. In this instance the heating was relatively brief, in order to learn whether its duration could be advantageously lessened. The reaction was evidently less complete than in experiments A and B.

In the subjoined table we give first the analysis of the natrolite itself, and then that of the leached residue from experiment B. In the latter we found that 0.86 per cent of silica was soluble in sodium carbonate solution, and that soda and lime remained corresponding to 4.61 per

* *American Journal of Science*, vol. ix., May, 1900.

cent of the original mineral. Deducting these impurities, together with the 0.42 per cent of hygroscopic water, and re-calculating to 100 per cent, we get the *reduced* composition of the residue. In the last column is given the calculated composition of an anhydrous ammonium-natrolite, $(\text{NH}_4)_2\text{Al}_2\text{Si}_3\text{O}_{10}$. This compound has evidently been formed to an extent represented by over 94 per cent of the leached natrolite residue. The agreement between theory, and even the unreduced analysis, is practically conclusive on this point.

	Natrolite found.	Residue found.	Residue $(\text{NH}_4)_2\text{Al}_2\text{Si}_3\text{O}_{10}$ reduced.	calculated.
SiO_2	46.62	53.71	53.86	54.06
Al_2O_3	26.04	29.94	30.52	30.43
CaO	1.48	0.34	—	—
K_2O	none	—	—	—
Na_2O	15.67	0.37	—	—
NH_3	—	9.26	9.85	10.14
H_2O at 100° ..	0.39	0.42	—	—
H_2O above 100°	0.18	5.94	5.77	5.37
	100.38	99.98	100.00	100.00

It may not be superfluous to note that the water given in the last two columns represents the difference between ammonia and the hypothetical ammonium oxide which has replaced soda.

Two other experiments upon natrolite remain to be noticed. First, the fresh mineral was boiled for fifteen minutes with a 25 per cent sodium carbonate solution; 0.72 per cent of silica dissolved. Similar treatment of ignited natrolite took out 0.62 per cent. No silica is split off by ignition. Ammonium-natrolite, before ignition, yielded 0.85 per cent of soluble silica, and after ignition 0.86 per cent. Here again no silica had been split off from the molecule, and practically none was liberated by the action of the ammonium chloride upon the natrolite. A simple, direct substitution of ammonium for sodium had occurred.

Scolecite.

On account of the well recognised analogy between natrolite and scolecite, the latter mineral seemed to be peculiarly worthy of examination. The specimen at our disposal was a mass of stout, radiating needles, which was collected by one of us at Whale Cove, on the island of Grand Manan, New Brunswick. Scolecite, we believe, has not hitherto been recorded from this locality, and on this account alone the material deserved attention.

Three sealed tube experiments were carried out, essentially as in the case of natrolite, as follows:—

- Heated ten hours at 350° . 13.74 per cent of lime and 0.35 of soda were taken out. The residue contained 8.78 per cent of ammonia.
- Heated ten hours at 370° . 12.97 of lime and 0.22 of soda were extracted. 8.48 per cent of ammonia in the residue. On account of the excessive temperature of this experiment, some reversion of the converted material had taken place.
- Heated five hours at 340° — 350° . Leach not studied. 8.91 per cent of ammonia in residue.

Analyses of the scolecite and of residues B and C are given below. The less perfect transformation in the case of B is evident.

	Scolecite.	Residue B.	Residue C.
SiO_2	45.86	53.39	53.69
Al_2O_3	25.78	30.51	30.50
CaO	13.92	0.62	0.42
Na_2O	0.41	undet.	0.29
NH_3	—	8.48	8.91
H_2O at 100° ..	0.40	0.74	0.12
H_2O above 100° ..	13.65	6.28	6.52
	100.02	100.02	100.45

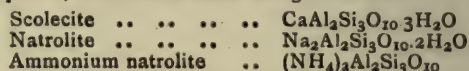
The product of the reaction is plainly the same as that obtained from natrolite, and the identity in type of the

two species is perfectly clear. This fact is further emphasised by an experiment upon the solubility of silica. The fresh scolecite gave up 0.36 per cent of silica to sodium carbonate solution, and the ignited mineral yielded only 0.50 per cent. Again, natrolite and scolecite behave in the same way.

Upon both minerals fractional determinations of the water were made, and the amount lost at each temperature was noted. The results, expressed in percentages of the original minerals, were as follows:—

Temperature.	Water lost.	
	Natrolite.	Scolecite.
100°	0.39	0.40
180°	0.40	0.52
250°	0.37	4.76
350°	8.51	0.55
Incipient redness ..	0.72	7.72
Full redness	0.12	0.04
Over blast	0.06	0.06
	10.57	14.05

Scolecite contains one more molecule of water than natrolite, and that amount, one-third of its total, seems to go off at a lower temperature than the other two molecules. Otherwise the two series of experiments are probably not far apart, and they indicate that the water is in neither case constitutional. The same conclusion is suggested by the existence of the anhydrous ammonium compound, the three formulæ being as follows:—



The parallelism is complete, and all three compounds are evidently salts of an acid $\text{H}_3\text{Si}_3\text{O}_8$, which is probably orthotrisilicic acid, $\text{Si}_3\text{O}_8(\text{OH})_3$. The second anhydride of this acid, $\text{H}_4\text{Si}_3\text{O}_8$, would be the ordinary trisilicic acid of orthoclase and albite, a relation which is certainly suggestive. We do not, however, care to enter upon the question of chemical structure in this paper, and we therefore leave the subject for fuller consideration at some future time. It is clear, however, that orthosilicate formulæ for natrolite and scolecite must be discarded.

Prehnite.

The prehnite taken for examination was an old specimen from Paterson, New Jersey. The analysis, with fractional water determinations, is given below.

Analysis.	Fractional water.	
	At 100°	At 180°
SiO_2	42.31	0.21
Al_2O_3	19.95	0.18
Fe_2O_3	6.20	0.10
FeO	none	0.11
CaO	26.63	Incipient red heat ..
H_2O	5.02	Full red heat
		Over blast
	100.11	5.02

With sodium carbonate solution, 0.38 per cent of silica was extracted from the fresh mineral. From the ignited prehnite 1.22 per cent was taken out. Very little silica, therefore, is liberated by ignition.

Two determinations were made of the action of ammonium chloride, as follows:—

- Heated eight hours. On leaching with water, 1.31 per cent of lime and 0.17 of alumina dissolved.
- Heated twelve hours. 1.41 per cent of lime was extracted, and in the washed residue 0.22 per cent of ammonia was found.

Prehnite, therefore, differs widely from natrolite and scolecite in its behaviour with ammonium chloride. Very little action takes place, even upon long heating to

350° in a sealed tube, and practically no ammonia is absorbed. The water is more firmly held than was the case with the other two minerals, and is almost certainly to be regarded as constitutional. The orthosilicate formula for prehnite is unaffected by these results, and may stand as fairly probable. Prehnite cannot be correlated with natrolite and scolecite on any basis of similar chemical structure.

Pectolite.

In the first paper of this series (*Amer. Journ. of Science*, October, 1899) we described a number of experiments upon pectolite, in which we showed that it was almost undoubtedly a metasilicate; but the action of ammonium chloride upon it was neglected, as having been studied already by Schneider and Clarke (*Bulletin No. 113*, "U.S. Geological Survey," p. 34). In their experiments upon pectolite from Bergen Hill, which was nearly identical in composition with our sample, a triple heating in an open crucible with ammonium chloride removed 20.50 per cent of lime, 6.95 of soda, and 0.54 of manganous oxide; or about two-thirds of the total amount of bases present. In our last paper we reported a preliminary experiment by the sealed tube method, and found that 20.72 per cent of lime and 6.46 of soda were taken out, while 1.44 of ammonia was retained by the residue. Here again two-thirds, approximately, of the bases had been converted into chlorides by the reaction. The open crucible and the sealed tube gave essentially the same results, although the retention of ammonia was not noticed by Schneider and Clarke.

In order to obtain further light upon pectolite we continued our experiments with the sealed tube method, and have obtained very variable results. All of the heatings with ammonium chloride were conducted at 350°, and the pectolite used was from the same Bergen Hill specimen which served us for our previous work. Our data are as follows, including, for convenience of comparison, the preliminary experiment which was cited above.

- A. Heated six hours. On leaching, 20.72 per cent of lime, 6.46 soda, and 0.11 alumina dissolved. The residue contained 1.44 per cent of ammonia.
- B. Heated six hours. - 20.10 per cent lime and 5.80 of soda extracted. 1.45 per cent ammonia in the residue. The residue was also examined for silica soluble in 25 per cent sodium carbonate solution (on fifteen minutes boiling), and 43.38 per cent was found.
- C. Heated six hours. Soluble portion neglected. The residue contained 2.23 per cent of ammonia and 61.79 per cent of soluble silica. The full analysis of this residue is given later.
- D. Heated ten hours. A complex breaking up of the pectolite took place, and leaching with water extracted the following percentages:—

SiO ₂ ..	..	..	..	5.43
Al ₂ O ₃	..	..	..	0.22
CaO ..	..	..	..	28.20
MnO ..	..	..	..	0.23
Na ₂ O ..	..	..	..	8.28

The residue from this leaching contained 39.63 of soluble silica, but ammonia was not determined.

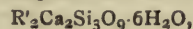
These results are so irregular that definite conclusions can hardly be drawn from them. A and B agree fairly with each other, and also with the earlier work of Schneider and Clarke. C contains more ammonia, but differs widely from B as to the amount of soluble silica in the residue. D, which represents a long heating, indicates a more complete reaction than was observed in either of the other cases.

An ammonium compound, however, is evidently formed during the reaction, although its precise nature cannot be determined from the evidence now in hand. Something may be inferred from the following figures, which are to be summarised thus:—First, we reproduce from our earlier

paper the analysis of the pectolite itself. Secondly, we give the analysis of the insoluble residue obtained in experiment C. The third column of figures is obtained by subtracting from the second column 61.79 of soluble silica and 1.18 of hygroscopic water, and re-calculating the remainder to 100 per cent. The fourth column contains the molecular ratios calculated from the third.

	Pectolite.	Residue found.	Residue reduced.	Ratios.
SiO ₂	53.34	75.98	37.74	0.629
Al ₂ O ₃	0.33	0.08	0.19	0.002
CaO	33.23	9.56	25.43	0.454
MnO	0.45	0.24	0.63	0.009
Na ₂ O	9.11	1.84	4.89	0.079
NH ₃	—	2.23	5.93	0.349
H ₂ O at 100° ..	0.27	1.18	—	—
H ₂ O above 100° ..	2.70	9.47	25.19	1.399
CO ₂	0.67	—	—	—
	100.10	100.58	100.00	

These ratios roughly suggest the formation of a salt approximating in composition to the formula—



in which R' is about two-thirds ammonium and one-third sodium. Pectolite itself has the formula $NaHCa_2Si_3O_9$; so that the existence of a hydrous ammonium pectolite is indicated—a conclusion which is probable, but not proved. The reaction between pectolite and ammonium chloride is possibly simple at first, but followed by or entangled with secondary changes which obscure the results. The experiments are interesting, however, as showing how widely pectolite differs from the other minerals which we have studied, as regards the ammonium chloride reaction. The general investigation is to be continued, and we hope to take up next the more important lime-soda zeolites.

NOTICES OF BOOKS.

Quantitative Chemical Analysis. By Dr. C. REMIGIUS FRESSENIUS, Privy Aulic Counselor, Director of the Chemical Laboratory at Wiesbaden, Professor of Chemistry, Physics, and Technology at the Wiesbaden Agricultural Institute. Seventh Edition. Translated from the revised Sixth Edition by CHARLES E. GROVES, F.R.S. Vol. II. London: J. and A. Churchill, 7, Great Marlborough Street. 1900.

WE are glad to announce that this valuable work is now complete. The publication has occupied some considerable time, but the fact that it has appeared in seven parts will partly account for this. The book is too well known to need much comment; no effort seems to have been spared to bring the work thoroughly up to date, and we have already referred to the various parts as they have been published. From Part II. it is not merely a new edition, but is in reality a new book. The "special part" includes the analysis of potable waters, mineral waters, technical products, and minerals, as well as the estimation of sugars, alcohol, tanning materials, and anthracene, the estimation of the inorganic matter in plants, the analysis of soils and manures, and the examination of atmospheric air. The revision of the second part afforded the late author of the book an opportunity of introducing the various analytical processes which had been published since the appearance of the former edition. Although the results of the re-determination of atomic weights have been embodied in the tables given at the end of the book we notice that the decomposition of didymium has been overlooked. This is a pity, as the determination by Brauner and others of the equivalents of its constituents

neo- and praseo-dymium have placed the matter quite beyond doubt. We note that lanthanum is called lanthanum, but this is probably a clerical error.

The exercises for practice at the end of the book, and also the tables for the calculation of analyses will be found of very great value. The book is plentifully and well illustrated, and there is a full table of contents and a copious index that will greatly facilitate its use.

CORRESPONDENCE.

XANTHATES OF NICKEL AND COBALT.

To the Editor of the Chemical News.

SIR,—Some chemists in the United States are, apparently, claiming to have discovered, in 1895, the easy method of separating nickel from cobalt by means of xanthate of potash, which method was discovered by me in 1877, and duly published in the *CHEMICAL NEWS* of that year.

Since the publication of my note ("Observations on some Xanthates: Separation of Nickel and Cobalt," 1877) I have replied to private correspondence, and given instructions on the subject to several chemists at home and abroad.—I am, &c.,

T. L. PHIPSON, Ph.D.

Casa Mia Laboratory, Putney, S.W.,
August 18, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

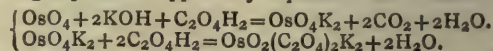
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 4, July 23, 1900.

Solubility of a Mixture of Salts having a Common Ion.—Charles Touren.—The author considers the two cases:—(1) Of the solubility of solid potassium nitrate in solutions of increasing concentration of potassium carbonate, and (2) of the solubility of potassium nitrate in solutions of increasing concentration of potassium bicarbonate. In the first case, the numbers prove that the dissociation of the nitrate and of the carbonate is not complete; the chloride and the carbonate only lower the solubility of the nitrate for mean concentrations. In the latter case, where the uncertainty of the nature and the number of the ions is greater than in the preceding case, the curve of solubility obtained appears to be decidedly above the curve relative to the chloride.

A New Complex Acid and its Salts, Pallado-oxalic Acid and Pallado-oxalates.—H. Loiseleur.—This paper describes four new bodies: pallado-oxalic acid and three of its salts—silver, sodium, and barium pallado-oxalates. The preparation of pallado-oxal-c acid is worthy of attention, as it is the only complex acid of palladium discovered up to the present time. Since the researches of Roessler, who vainly tried to isolate pallado-hydrocyanic acid, palladium was reputed incapable of forming complex acids and as a conclusion from this, appeared to possess only in a very slight degree the metalloidic character which platinum shows decidedly in so many of its combinations. The present research shows that this is not true. It is even apparent that this metalloidic character is more marked in palladium than in platinum, since pallado-oxalic acid can be obtained in very well-formed crystals, whilst the corresponding platinum, plato-oxalic acid, has only been obtained by Söderbaum in the form of a confused crystalline mass.

Some Osmyloxalates.—L. Wintrebert.—When excess of oxalic acid acts on a potash solution of OsO_4 , a new salt is formed which acts on polarised light. During the course of this reaction, when large quantities of CO_2 are evolved, a violet colouration is apparent, which is characteristic of potassium osmate, OsO_4K_2 . By adding oxalic acid to an alkaline concentrated solution of potassium osmate, the liquid, when slightly heated, passes from dark red to clear brownish yellow, and on cooling deposits brown needle-shaped crystals. Analysis shows these crystals to have the formula $\text{OsO}_2(\text{C}_2\text{O}_4)_2\text{K}_2 \cdot 2\text{H}_2\text{O}$, and is a hydrated osmyl-oxalate of potassium. The following equations apparently represent the reaction:—



An osmyloxalate of sodium was also prepared.

Action of various Finely-divided Metals (Platinum, Cobalt, and Iron) on Acetylene and Ethylene.—Paul Sabatier and J. B. Senderens.—In a previous paper the authors showed that recently reduced nickel acts directly on acetylene, either slowly or with incandescence. With platinum black, iron, or cobalt the slow reaction is scarcely perceptible, and the phenomenon is limited to the decomposition with incandescence followed by the more or less complete hydrogenation of a portion of the acetylene. Ethylene, on the other hand, is rapidly decomposed above 300° by recently reduced nickel. The metal swells up considerably and evolves a variable mixture of methane, ethane, and hydrogen accompanied by a very slight proportion of higher formenic carbides.

Synthesis of Paramethoxyhydratropic Acid.—J. Bougault.—This acid has been synthesised already by M. Trinius, but owing to some errors the synthesis has been again undertaken by the author, who arrives at the following conclusions:—(1) M. Trinius made an error in identifying with phloretic acid the paraoxyhydratropic acid which he had obtained synthetically, starting from atropic acid. (2) This paraoxyhydratropic acid is identical with that which results from the demethylation of the acid which the author prepared when starting from anethol. (3) The derived acid of anethol is paramethoxyhydratropic acid.

Influence of Hydrobromic Acid on the Velocity of the Reaction of Bromine on Trimethylene.—G. Gustavson.—Hydrobromic acid possesses the remarkable property of exciting the reaction between trimethylene and bromine. The author examines this reaction quantitatively.

Organic Solutions of Iron Perchloride.—Echsner de Coninck.—When organic solutions of Fe_2Cl_6 are filtered through animal charcoal under certain conditions, it is observed that the water, even when present in small proportion, exercises a decomposing action which is brought into play by the animal charcoal. Methyl alcohol acts in the same way, and is in a manner more efficacious than when it is present in larger quantities. Organic liquids, which do not contain either water or methyl alcohol, simply dissolve the iron salt, and a very long time is necessary to produce even a slight decomposition of the chloride.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 7.

This number contains no fresh matter of chemical interest.

No. 8.

Preparation of Fluorine by Electrolysis in a Copper Vessel.—H. Moissan.—Already inserted in full.

Production of Ozone by the Decomposition of Water by means of Fluorine.—H. Moissan.—Already inserted in full.

Action of Hydrofluoric Acid and of Fluorine on Glass.—H. Moissan.—Already noticed.

Volume Composition of Hydrofluoric Acid.—H. Moissan.—Already noticed.

The Constitution of Isolauroic Acid.—G. Blanc.—Already noticed.

An Acid Dihydrodisulphone Derivative of Carvone.—H. Labbé.—It has been supposed up to the present that carvone was not susceptible of forming a combination with the alkaline bisulphites. Recent examples have, however, shown, in the aldehydic series, that the non-saturated bodies of this class possess the power of fixing, besides the normal molecule of bisulphite, one or two other molecules which become attached to the double bonds of the substance. The author has shown that certain cyclic ketones give relatively very stable compounds, which are not decomposed by acids or alkalis. Carvone is one of these, and it is easy to prepare a dihydrodisulphone derivative from this ketone. The carvone is treated at the boiling temperature in a flask fitted with a vertical condenser with a solution of commercial bisulphite of soda with enough dry carbonate of soda added to remove the sulphurous acid. At the end of three-quarters of an hour the ketone is entirely dissolved. To isolate this dihydrodisulphone derivative, the aqueous solution is evaporated almost to dryness on the water-bath, taken up with alcohol, boiled again, and filtered rapidly in a warm funnel. The evaporated alcoholic solution is again taken up with alcohol at 97–98°, filtered, and evaporated a third time; taken up again with alcohol as before, and finally evaporated quickly to dryness in vacuo. The dihydrodisulphonate of sodium carvone is thus obtained in the form of a white or yellowish white powder, which is very deliquescent; its composition is found on analysis to be $C_{10}H_{16}O_7S_2Na_2$.

Rapid Method for the Estimation of Carbonic Acid in different Gases.—L. Vignon and L. Meunier.—Already noticed.

An Apparatus for Measuring Disengagements of Gas at a Constant Volume.—A. Job.—This new gasometric apparatus is based on the following principle:—A closed vessel of constant volume is furnished with a pressure gauge. If, in the interior of this closed space, we produce a reaction which gives off a gas, and we bring the apparatus back to the original temperature, the excess of pressure, reduced to 0°, will be proportional to the mass of the gas given off. A special arrangement enables us to bring bodies with which we wish to react in contact with the gas by means of an exterior manipulation which does not alter the gaseous mass contained in the apparatus. A description of the apparatus follows, which requires the accompanying figure to be properly understood. By means of this apparatus estimations of carbonates can be made with great exactitude, and, from a practical point of view, it has an important application in the estimation of ammoniacal salts, and of urea by the disengagement of nitrogen. As a ureometer, for which purpose a special pattern has been designed, it has already been of great service.

New Electrodes for Electrolytic Estimations.—A. Hollard.—This apparatus cannot be properly described without the accompanying diagram; it has, however, the advantage of giving a deposit of regular thickness on both the interior and exterior of the cone-shaped electrode, with an increase of speed in the formation of the deposit. The gas is given off throughout the mass of the liquid, and thus losses by projection are less to be feared, and at the same time a much stronger current can be used than is generally the case.

Analysis of Commercial Copper.—A. Hollard.—Already inserted in full.

The Localisation, Elimination, and Origin of Arsenic in Animal Tissues.—A. Gautier.—Already noticed.

Estimation of Arsenic in Metals and in Alloys.—A. Hollard.—Already inserted in full.

Reversible Liquefaction: a New Physico-chemical Property of Albumenoid Substances.—M. Tsvett.—Already noticed.

Journal de Pharmacie et de Chimie,
Series 6, Vol. xi., No. 12.

Santalenes and Santalols.—M. Guerbet.—When heated to 180–190° in sealed tubes with acetic acid (fusing-point 16°), the α and β santalenes combine very slowly with the acid, giving acetates of santalene. After heating for 120 hours only 1.25 grms. of acetate of santalene α is obtained from 50 grms. of the carbide and 20 grms. of acetic acid. If a current of dry hydrochloric acid gas is passed through an ethereal solution of the santalenes, cooled with a mixture of ice and salt, two liquid hydrochlorates are obtained answering to the formula $C_{15}H_{24}HCl$. These hydrochlorates cannot be distilled, even in vacuo, without decomposing. Both the α and β santalenes combine with the chlorides of nitrosyl, giving nitrosochlorides with the formula $C_{15}H_{24}NOCl$. The different properties of the santalenes show that they are sesquiterpenes. The α and β santalols are both primary alcohols, their speeds of etherification are 41.7 for the isomer α and 43.6 for the isomer β , their limits of etherification are 68.5 for the α santanol and 69 for the β santanol. This fact is interesting, as all the terpenic or sesquiterpenic alcohols known up to the present have been regarded as secondary or tertiary alcohols.

MISCELLANEOUS.

Reduction of Tungstic Anhydride by Zinc. Preparation of Pure Tungsten.—Marcel Delépine.—The reduction of tungstic anhydride by means of zinc allows of the easy preparation of pure tungsten at temperatures below that at which zinc distils. In physical properties, the metal thus prepared possesses the density and heat of combustion of crystalline or ordinary tungsten. It can also, by compression or trituration, be made to assume the brilliance of metals. In fact, it can be positively asserted that this substance acts as an identical element, though prepared in a state of fine division due to the slight fusibility of tungsten.—*Comptes Rendus*, cxxxi., No. 3.

The Use of Alkaline Chlorides in the Absorption of Phosphide of Hydrogen, and on a Method for the Purification of Raw Acetylene based on this use.—C. Goettig.—The purification of raw acetylene is generally carried out by passing the gas through saline solutions which absorb the PH_3 , NH_3 , SiH_4 , CO , &c. In such cases the formation of a detonating metallic acetylide is to be feared; therefore these solutions, which are, further, easily exhausted, are made strongly acid. The author, by adding an alkaline chloride to these solutions, increases the time of their use, and, moreover, permits the use of neutral solutions. For example, a solution of ferric nitrate, sulphate of copper, or mercuric nitrate, acidulated with nitric acid, becomes cloudy after passing about 600 c.c. of raw acetylene. After the addition of about 40 per cent of chloride of potassium, it takes 2600 c.c. of the gas to make the solution cloudy. A non-acidulated solution of mercuric chloride becomes cloudy after passing 1200 c.c. of the raw gas; after the addition of KCl it takes nearly 6000 c.c. of the gas to produce a cloudiness. We see that the use of KCl has prevented the formation of a metallic compound for a considerable time without the use of nitric acid.—*Berichte*, vol. xxxii., p. 1879.

Preparation of Antitoxin from Antidiphtheritic Serum.—E. Freund and C. Sternberg.—After having shown, in this note, the action of a large number of alkaline salts, or of salts of the heavy metals, on antidiphtheritic serum, from the point of view of the precipitation and the destruction of the antitoxin, the authors propose the following method for the preparation of this antitoxin. The serum is treated with one-third its volume of a solution of potash-alum at 5 per cent; the precipitate formed is collected by filtration; the alum is removed from the filtrate by dialysis, which is then thrown on a filter to remove the slight precipitate formed during the dialysis; it is then treated with an equal volume of a saturated solution of sulphate of ammonia. The precipitate formed is re-dissolved, submitted to prolonged dialysis, and concentrated in vacuo. In this manner we can obtain, from half a litre of serum, about 9 grms. of a dry, brownish, gelatinous residue, possessing antitoxic properties, completely soluble in water or in physiological salt water.—*Zeit. f. Hygiene*, vol. xxxi., p. 429.

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THE CHEMICAL NEWS.

Vol. LXXXII., No. 2127.

ON THE ANALYSIS OF CHROME-IRON ORE BY THE BORAX METHOD.

By R. W. EMERSON MACIVOR, F.I.C., &c.,
Formerly Assistant-Professor of Chemistry, Anderson's College,
Glasgow.

OVER a quarter of a century ago the late Professor Dittmar and myself had occasion to make complete analyses of numerous samples of chromite, and at first employed the acid sulphate of potassium process to effect the decomposition of the ore, but soon abandoned it in favour of a modification of the then generally neglected borax process. In later years, long after my professional connection with him had ceased, Dittmar further improved this process, and it is a matter of some surprise to me that the details of his method should be absent from the pages of our principal laboratory text-books. The process is not only an eminently practical one for commercial purposes, particularly when complete analysis of the ore is required, but, in my opinion, forms a good quantitative exercise for the analytical student.

I am prompted to send this note for publication in the CHEMICAL NEWS through having read R. Fieber's recent paper on "A Simple Method of Decomposing Chromite" (*Chem. Zeitung*, xxxiv., 333, and *Amer. Journ. Sci.*, 1900, vol. x., No. 55), in which the borax process is recommended for the purpose indicated in the title of the paper.

Fieber's manner of fluxing his chromite is briefly as follows:—0.5 gm. of the finely powdered ore is fused in a platinum crucible with 3 grms. of sodium-potassium carbonate, for ten minutes; when cold, 3 grms. of dry borax are introduced, and the whole is again fused by first heating for a short time over the flame of a Teclu burner, and then for forty-five minutes over the blowpipe. If the decomposition is not then complete, a further quantity of the mixed carbonates should be added and the operation of fusing repeated.

I fail to see any material difference between Fieber's method and that described in text-books which I may now call ancient, and, on his own showing, it possesses the same defects, the chief of which is uncertainty as to the number of fusions necessary to effect the decomposition of the ore. Now in Dittmar's improved borax process there is no doubt on this score, provided, of course, the ore is rendered impalpable and the manipulations carried out in accordance with his directions. The experience of many years, with chrome ores from all parts of the world, enables me to confirm—if confirmation be at all necessary—Dittmar's own statement: "Undecomposed ore rarely exceeds 2 m.grms. (per gm. of ore = 0.2 per cent) if the fusion be carefully conducted. Such small quantities may be taken into account as containing 50 to 60 per cent Cr_2O_3 without serious error."

The main feature of the Dittmar process is the use of a flux composed of equal weights of borax glass and the carbonates of potassium and sodium (the latter mixed in the proportions of their molecular weights) prepared beforehand by melting the components together in a platinum dish or crucible, and pouring out the melt on a suitable polished surface. The flux is broken up into pieces, and, being somewhat hygroscopic, should be kept in well-stoppered bottles. I have at times varied the composition of this flux, but the relative proportions have never been greater than 3 parts of KNaCO_3 to 2 parts of borax. This mixture gives a flux of more "pasty" consistency,

and therefore better able to keep the ore in suspension during fusion, thereby facilitating its decomposition.

It would not, of course, be permissible in a contribution like the present to enter into the full details of Dittmar's process for the complete analysis of chromite, but as few, if any, of our analytical works refer to it at all, perhaps the particulars of its first stage may be of interest to some of the readers of this journal:—Fuse 4 grms. of the flux in a platinum crucible over an Iserlohn lamp, allow to solidify, and put on the top of the fuse about 0.5 gm. of the ore, which must be in an impalpable condition. Heat the crucible with the lid on until the flux has quite melted and the ore sunk to the bottom. The lid is then taken off, the crucible placed at an angle on a triangle, and the lid in front of it horizontally; heat is again applied, and the contents of the crucible kept in motion by aid of a thick platinum wire until the ore is dissolved. If the lamp is in good order and the gas pressure high, it will not be necessary to have recourse to the blowpipe. After half an hour's heating the whole of the Cr_2O_3 can be assumed to have passed into the state of alkaline chromate. The contents of the crucible are allowed to cool to solidification, 2.5 grms. Na_2CO_3 added, and the whole again fused. The fuse is poured into a platinum dish, and the crucible freed from adhering matter by heating in water contained in a porcelain basin, and thorough washing. To this solution the bulk of the fused mass is added, and the whole allowed to stand on a water-bath until disintegration is complete; filter, wash with hot water as long as the runnings are yellow.

When a complete analysis is contemplated it is well to start with a gm. of ore. This involves the use of twice the quantities of flux and Na_2CO_3 recommended for 0.5 gm. of ore.

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GADOLINIUM.

By EUG. DEMARCAY.

GADOLINIUM, discovered by Marignac, and which M. Lecoq de Boisbaudran characterised by its beautiful band spectrum (*Comptes Rendus*, cxi., p. 472), has since been the object of researches by Bettendorf (*Liebig's Annalen*, cclxx., p. 376), and recently by Benedick (*Zeit. f. Anorg. Chem.*, xx-i., p. 393).

The gadolinium used in these researches contained manifestly, besides small quantities of terbia, shown by the yellow colour of the oxide (which is white in the pure state), a certain quantity of $\Sigma\text{-Z}_e$, which they have not eliminated.

During the course of my fractionations I isolated a decided quantity of double nitrate of magnesium and gadolinium. The spectrum of the gadolinium extracted from this salt, examined under the spark of my induction coil, only showed slight traces of the strong lines of $\Sigma\text{-Z}_e$ and yttrium. The stronger lines of this spectrum are only feeble; I estimated these traces of yttrium at less than 1/10,000th part. In the absorption spectrum, absolutely nothing is visible between 3500 and the red end when a layer of 15 c.m. thick of melted nitrate is used, and the same on reversion.

This gadolinium at first sight appears to be as white as magnesia, but with a little attention slight yellow tinges may be seen. This faint tint probably shows the presence of a trace of terbia, for these two earths are very difficult to separate; the other salts are colourless. The double magnesium nitrate melts at 77.5–78°. The simple nitrate, crystallising with 6H₂O, melts about 91.5–92°. This last number is a little uncertain; at this temperature the nitrate with 6H₂O seems to lose water and be transformed into a less hydrated nitrate, which remains in solution and may lower the fusing-point:

This gadolinium gives the band spectrum of M. Lecoq de Boisbaudran. This method of spectrum examination is, however, not so reliable for this research as the photographic method of the line spectrum. Between the limits $\lambda=4800$ and $\lambda=3500$ the principal lines of this spectrum, which have not been described before, are as follows:—

λ .	Strength.	λ .	Strength.
4583.1	7 (a)	3867.3	7
4522.5	7	3863.2	6
4346.8	10	3852.6	11
4342.3	9	3844.8	9
4316.5	6	3842.5	9.5
4296.8	10	3840.0	8
4281.1	9	3837.3	7
4262.9	11	3835.2	7
4252.7	8	3827.6	6
4239.8	7	3817.0	6
4230.9	6	3814.2	10
4218.4	7	3805.6	9
4216.2	7	3796.8	11
4213.0	8	3792.8	8
4205.8	7.5 (b)	3791.5	8
4198.6	8	3788.1	8
4191.8	8	3782.7	9
4184.8	10	3771.2	9
4176.2	6	3768.9	11
4163.3	6.5	3764.8	7
4155.3	6	3761.3	6
4140.9	6	3744.0	10
4137.3	8	3740.6	7
4132.4	10	3733.6	7
4130.3	11 (c)	3731.4	7
4111.6	7	3719.9	9
4098.6	13	3713.1	8
4093.8	6	3698.1	7
4087.7	6.5	3671.4	7
4085.7	9	3664.7	10
4078.3	10	3662.4	6
4073.7	10	3656.3	8
4070.4	8	3654.7	8
4063.4	9	3651.1	6
4058.2	6	3646.3	11
4053.7	9	3634.6	6
4049.8	12	3624.9	6
4039.7	8	3617.1	6
4037.6	9	3613.4	6
4028.2	7	3610.9	7
4023.4	6	3608.8	6.5
4013.9	7	3600.9	6
4009.1	8	3592.6	7
4005.2	7.5	3584.9	9
4001.6	6	3581.8	7
3994.4	6	3578.3	6
3987.9	6.5 (d)	3574.7	6
3974.7	6	3571.8	6
3959.9	10	3558.2	7
3958.0	9.5	3557.0	7
3916.7	10	3549.3	10.5
3902.6	8	3545.7	10
3886.1	9	3542.6	6
3895.0	9	3511.7	9

- (a). Near to a strong line of $\Sigma-Z_e$.
 (b). Coincides with a strong line of $\Sigma-Z_e$.
 (c). Coincides with a strong line of $\Sigma-Z_e$.
 (d). Very near to a strong double line of ytterbium.

The maximum of strength for this scale is 16 and the minimum 1.

In this spectrum the most persistent lines are 3549.3 and 3545.7, and these, with the other strong lines of the spectrum, constitute a good reaction for gadolinium. This reaction, although very inferior in sensibility to that for yttrium, ytterbium, and $\Sigma-Z_e$, allows of the detection of gadolinium directly in almost all crude rare earths.

The atomic weight of gadolinium has been found to be about 155 by the various chemists who have investigated the properties of this element. From several attempts I have also found a number approximately the same. I believe it to be slightly too high, in consequence of the defects of the method (synthesis or analysis of the anhydrous sulphate) used by myself and all the other observers.—*Comptes Rendus*, cxxxi., No. 5.

ATOMIC WEIGHT OF RADIO-ACTIVE BARIUM.

By M^{ME}. CURIE.

THROUGHOUT our researches on the isolation of radium, the progress of the concentration of this element has been controlled by examination of the spectrum, and by determinations of atomic weights.

Each time that a quantity of radiferous barium chloride was obtained from the mineral, I submitted this chloride to a systematic fractional crystallisation to extract several decigrams of a product containing more concentrated radium. By adding to the solution of this product a little alcohol, or better, a little hydrochloric acid, until a slight precipitate forms, I obtained one or two centigrams of a still more concentrated product, which was used for the spectrum examination. The remaining product served for the determination of the atomic weight of radiferous barium.

The investigation of the spectrum of the successive products has been undertaken by M. Demarçay, who has published his results. The last of these products apparently only contains a trace of barium, and may be considered as almost pure radium chloride.

The isolation of radium chloride has therefore been obtained, but the quantity of pure salt isolated is insufficient for the determination of the atomic weight of radium. I had to be content with determining the atomic weight of radiferous barium with the less concentrated product, of which I had 0.4 grm.

The last analogous determination, which I made several months ago, gave for the atomic weight of radio-active barium the number 146, which already is decidedly higher than 137.5, the atomic weight of pure barium.

The method now employed was the same. It consists in the estimation of the chlorine in the anhydrous chloride. A determination was simultaneously made on pure crystalline barium chloride under exactly the same conditions, this latter serving as a control experiment. The pure barium chloride was weighed in a crystalline state, also in the anhydrous state; the radio-active barium chloride only in the anhydrous state.

After being kept at a temperature of 130° for an hour, the two salts lose all their water of crystallisation; after this their weight remains constant, however long the heating is continued. Even if the temperature is raised to 150°, and kept so for an hour or more, no further loss of weight is observed, and this indicates that there is no loss of chlorine.

This last determination gives 138.0 as the atomic weight for barium in pure barium chloride, whilst the two determinations carried out on the radio-active chloride give 174.1 and 173.6 as the numbers for the atomic weight of the metal in this chloride. We have no means of distinguishing the relative quantities of radium and barium in this product. M. Demarçay thinks, however, from the aspect of the spectrum, that there is rather more radium than barium. In any case it is certain that the atomic weight of radium is much higher than 174.

The quantity of radium chloride that I have isolated is insufficient to make an examination of the properties of pure radium. However, M. Curie and myself are very pleased at having obtained a proof of the existence of this

element, and so having confirmed the ideas which guided us in our researches on radio-active materials.—*Comptes Rendus*, cxxxi., No. 6.

THE FOSSIL FLOUR OF SANTAFIORA.

By G. DE NEGRI.

FIFTY years ago G. Fabroni proposed the manufacture of light bricks similar to those made by the ancient Romans, and which, according to Pliny, Vitruvius, and Strabo, had the property of floating on water. The material used by M. Fabroni for making his refractory bricks was the fossil flour (Berg-mehl) of Santafiora.

The bricks, prepared by the firm of Rimbotti and Hemmeler by means of this flour, which exists in large quantities in the district of Monte Amiata, are used for lining ovens.

Although these bricks resist a very high temperature without melting, they have the drawback of not possessing sufficient strength to resist the mechanical action of the materials melted in metallurgical furnaces.

The fossil flour of Santafiora is composed as follows:—

Water and organic matter		12.40
Silica		82.00
Alumina and oxide of iron		4.20
Lime		0.55
Magnesia		0.45
Undetermined and loss		0.40

By calcining at a red heat it loses 12.40 per cent, from which must be deducted 4.70 per cent of water driven off at 100°.

The calcined fossil flour has therefore the following composition:—

Silica		93.16
Alumina and oxide of iron		4.79
Lime		0.62
Magnesia		0.51
Undetermined and loss		0.92

This fossil flour, by its state of extreme division, by its porosity, and by its richness in silicic acid, is easily attacked by the alkalis, and can be used for the manufacture of silicate of potash and silicate of soda (soluble glass).

This operation, at the ordinary pressure, is fairly long, but if alkalis of 1.2 to 1.3 density are used under a pressure of about three atmospheres for two or three hours, we obtain a soluble glass which is richer in silicic acid than that prepared by the use of silica.

The natural fossil flour is more readily attacked by alkaline solutions than that which has been calcined, but the glass obtained by means of this latter, for the same amount of alkali, contains more silica, as the raw fossil flour loses water and organic matter by calcination, and the quantity of silicic acid thus remains higher.

With natural fossil flour we obtained a soluble potash glass, which contained three parts of silica for two parts of potash. With soda we obtained a glass containing equal parts of alkali and silicic acid.

The same experiment has been repeated with fossil flour calcined at a red heat. With potash lye it gave a soluble glass which, for one part of potash, contained 1.9 of silica; that prepared with soda was formed of one part of alkali and two parts of silicic acid.

The soluble glasses obtained with this material are of excellent quality. They will bear comparison not only with those prepared by fusion, but also with the soluble glasses manufactured by Kuhlmann's process.

Fossil flour should be calcined at a high temperature, on account of its low density and its large volume. As it is a very bad conductor of heat the operation is excessively

long, and it is for this reason that the use of this material has been abandoned.

However, the new methods of calcination due to Grūnc and Hagemann have considerably reduced the cost of calcined fossil flour, to such a point even as to render its use possible for the manufacture of soluble glass.

In the Monte Amiata district we also meet with another variety of fossil flour with a slight yellow colour, which is less porous and a little more compact than the other, but of a somewhat similar composition:—

Water and organic matter		12.90
Silica		80.32
Alumina and oxide of iron		5.17
Lime and magnesia		0.74
Carbonic anhydride		0.55
Undetermined and loss		0.32

It loses 7.37 per cent by calcination, after making the necessary deduction for water lost at 100°.—*Moniteur Scientifique*, Series 4, vol. xiv., July, 1900.

THE DETECTION OF NITROGEN IN ORGANIC SUBSTANCES CONTAINING SULPHUR.

By E. TAUBER.

ABOUT twenty years ago O. Jacobsen proposed a method for the detection of nitrogen in organic substances containing sulphur, consisting of adding to the substance under examination at least four or five times its volume of iron filings before heating with metallic potassium. The object of adding the iron was to transform the sulphocyanate of potassium, which was formed in the presence of nitrogen and sulphur, into cyanide of potassium and sulphide of iron.

Jacobsen's method is still considered to be good, and is still used by chemists. I was therefore astonished to find a few months ago that the addition of iron might lead to the greatest errors in the search for nitrogen in organic matters. For this reason, and also because it is entirely superfluous, the use of iron ought to be completely stopped.

At the temperature of the reaction, finely divided iron has the property of fixing the atmospheric nitrogen to such a large extent, that under the conditions laid down by Jacobsen cyanide of potassium is formed, even though the substance examined is quite free from nitrogen. I was made aware of this fact while looking for nitrogen in an organic substance containing a very small quantity of sulphur.

While in the absence of iron the substance hardly gave a faint blue colouration, the test repeated in the presence of iron furnished a voluminous precipitate of Prussian blue. It seemed very improbable that a trace of sulphur could mask such a considerable quantity of nitrogen, and the idea immediately occurred to me that the iron might have effected the fixation of the nitrogen and the formation of cyanide of potassium. Experiments fully confirmed this supposition, and showed, further, that all kinds of iron exercised the same influence from the qualitative, if not the quantitative point of view, on the formation of cyanide.

Even pure iron, free from nitrogen, obtained by the reduction of pure oxide of iron by hydrogen causes the formation of cyanide of potassium, when heated with organic substances, equally free from nitrogen. In this case the fixation of atmospheric nitrogen is beyond all possible question, while when we use impure iron containing nitrogen a portion of the cyanide formed may be due to the iron.

If, for the prevention of the access of air, we pass a current of hydrogen over the mixture containing pure iron during ignition, the formation of cyanide does not take

place. The proportion of cyanide formed naturally depends on the quantity of iron used, and the duration of the heating. In this manner a mixture containing very little iron, and heated for a comparatively short time, may not form any cyanide of potassium at all.

It is evident that Jacobsen had adopted this precaution—the limitation of the time of heating—without recognising its importance. It is only in this way that we can explain the fact that he did not detect the source of error caused by the use of the iron. On the other hand, the reduction to a minimum of the duration of the heating offers another danger; for the nitrogen, even when chemically combined, is not often transformed into cyanide until after an energetic and prolonged heating.

I am of the opinion that, as a rule, the formation of cyanide from nitrogenous organic matters takes place more rapidly than in the case of the atmospheric air constituting the exclusive source of the nitrogen.

From this it results that Jacobsen's method cannot give results worthy of belief, except when the mixture is heated long and vigorously in a current of pure hydrogen.

We should be all the more willing to dispense with this new complication, seeing that the use of iron for the detection of nitrogen in organic substances containing sulphur is entirely superfluous. Graebe (*Berichte*, vol. xvii., p. 1178) has already shown that the use of iron can be suppressed in this class of assay by slightly increasing the amount of metallic potassium used.

By a series of experiments I made certain that the statement made by Graebe was correct, and that when rationally employed the method always gave good results.*

If the substance contains a large proportion of sulphur, as well as a small quantity of nitrogen, the sulphide of potassium formed naturally reduces the oxide of iron added, and on the addition of acid we should obtain, in this case, not Prussian blue, but a cloudiness or bluish-white precipitate. The precipitate might consist of sulphur. To remove all doubt on this point, excess of ferric chloride should be added. The precipitate should then immediately take an intensely blue colour if ferrocyanide is present.

It is not therefore at all necessary to modify Lassaigne's method in the case of an organic substance containing sulphur. The employment of potassium in excess is useful in every case, even in the absence of sulphur.

The fact that metallic iron has the property of fixing atmospheric nitrogen, decided me to institute experiments with the object of determining whether it was not possible to base a technical method for the preparation of alkaline cyanides by means of the nitrogen of the air, on this property of iron, by substituting for the alkaline metals themselves their hydrates or carbonates, which are much less expensive. The experiments have given positive and, in a measure, such satisfactory results, that I consider the industrial use of this process not only as possible, but, further, as very probable. Certainly the results are rather variable, but I have finally succeeded in transforming with practical certainty 10 per cent of the soda used into cyanide of sodium. In some cases the return reached as much as 25 per cent.

However, in studying the bibliography of the question, I learnt that the same process had already been patented in the year 1880. The patents, belonging to Victor Adler (*German Patents*, Nos. 12351, 18945, 24334, and 32334), lapsed after six years, which shows that the process in-

volves considerable technical difficulties. In any case, basing my remarks on my own personal observations, I am still of the opinion that the process is capable of industrial application.

It may be noted in passing that no treatises or technical handbooks mention the Adler patent, while they devote a good deal of space to other much less practical attempts to utilise the atmospheric nitrogen for the manufacture of cyanides. However, it is incontestable that the atmospheric nitrogen is fixed in considerable proportions by a mixture of soda or potash and carbon in the presence of metallic iron, and that, at temperatures at which in the absence of iron the same mixtures do not give a trace of cyanide.

It is possible that, without having been aware of it, we have long utilised this particular property of iron in the manufacture of cyanide of potassium from nitrogenous scraps.

In this process we add iron to the mixture to combine with the sulphur, and thus protect the iron vessels in which the fusion takes place. But this addition of iron has probably the effect of converting into cyanide a part of the nitrogen of the scraps, which is always lost in considerable quantities during the operation.

I would further remark that among the other metals which I have tried for this purpose, no other has, to any pronounced degree, any analogous action to that of iron. I have tried copper, nickel, chromium, tungsten, and magnesium. The influence of magnesium, even in small quantities, was the most marked; then came tungsten, chromium, and nickel, and finally copper, which had no action at all at any temperature tried.

Experiments.

A. Experiments which show the Defects of Jacobsen's Method.—In all the experiments I used about 0.02 gm. of the substance and 0.2 gm. of potassium, first without iron, and then with the addition of about 0.5 gm. of iron obtained by the reduction of pure ferric oxide by hydrogen.

In some cases I made further experiments with smaller quantities of iron.

The reaction never occurred in the absence of iron, but was very pronounced in the presence of 0.5 gm. of iron after one to two minutes' heating.

The diminution of the proportion of iron had the result of diminishing the quantity of Prussian blue produced. On calcining the mixture for a very short space of time, say a quarter of a minute, the reaction does not take place, even in the presence of iron. These results were obtained with the following substances: milk sugar, sugar charcoal, hydroquinone, β -naphthol, salicylic acid, phthalic anhydride, anthraquinone, and the α - and β -naphthalene-sulphonates of soda. Crystallised methylsulphonate of potassium behaved in a slightly different manner.

With 0.05 gm. of iron this salt gave no colouration, but with 0.5 gm. of iron the blue colouration obtained was very pronounced, though without being intense. The cause of this phenomenon rests, no doubt, in the fact that this substance has but little tendency to set carbon at liberty under the conditions of the experiment.

B. Experiments which show the Defects of the Lassaigne Method, even in the Presence of Sulphur.—In these experiments we also used 0.02 gm. of material and 0.2 gm. of potassium. An appreciable blue colouration, augmented by the addition of ferric chloride, was always obtained; in most cases a strong colouration is produced directly. I have examined the following bodies:—Taurine, allylsulphocarbamide, sulphocarbamide, thioparatoluidine, benzidinesulphone, sulphanilic acid, naphthionate of soda, mixtures of equal parts of sulphanilic acid and sulphur, of equal parts of naphthionate of soda and sulphur, methylene blue mixed with one part of 2-amido-8-oxynaphthalene-6-monosulphonic acid and two parts of 1-oxynaphthalene-4:7-disulphonic acid, sulphonylsulphanilic acid, and, finally, a number of colouring

* I used about 0.02 gm. of the substance and 0.2 gm. of freshly cut potassium, and heated this carefully in a test-tube in such a manner that the metal became fused, and enveloped the substance as completely as possible. It was only then that I heated vigorously while rotating the test-tube, which is, as a rule, bent slightly out of shape under the action of the heat. To extinguish the melted mass I used 5 or 6 c.c. of water. It is because the mixture of the substance and the metallic potassium is heated too rapidly, and for too short a space of time, that mistakes in the analysis are most often made.

materials derived from triphenylmethane and azoics containing sulphur.

In none of these cases was the result doubtful, in spite of the presence of large quantities of sulphur in proportion to the nitrogen. Jacobsen's assertion to the contrary, that most of the organic substances containing sulphur as well as nitrogen will not give the Lassaigne reaction, cannot be explained by the fact that Jacobsen used too small quantities of metallic potassium. As Graebe has shown the reaction does not always succeed in these cases.

The experiments undertaken, with a view to the utilisation of finely divided iron for the fixation of the atmospheric nitrogen and the manufacture of alkaline cyanides, will form the subject of a future publication.—*Berichte*, vol. xxxi., p. 3150.

THE ESTIMATION OF ZINC AS PHOSPHATE.

By H. D. DAKIN.

THE original process for the estimation of zinc depending on the formation of zinc ammonium phosphate was first proposed by Hugo Tamm (*CHEM. NEWS*, xxiv., p. 148), and has since undergone comparatively few modifications.

Of papers published since the method was first devised perhaps the most important is that by M. Austin ("The Double Ammonium Phosphates of Beryllium, Zinc, and Cadmium in Analysis," *Amer. Journ. Sci.*, vol. viii., Sept., 1899), in which full analytical data are given. (No analyses of pure substances of known composition are given in Tamm's or in most other papers on this subject). The main conclusion drawn from the results is "that the presence of ammonium chloride is essential for the conversion of the zinc phosphate precipitated by hydrogen sodium ammonium phosphate to the ammonium zinc salt." Tolerably accurate results were only obtained when at least 10 to 30 grms. of ammonium chloride were present. The object of the present paper is to show that under somewhat different conditions this large quantity of ammonium salts is quite unnecessary; to point out, and if possible remove, certain small sources of inaccuracy; and to give test-analyses, showing that, with the prescribed conditions, good results may be obtained when weighing either as zinc ammonium phosphate or pyrophosphate.

Tamm, though strongly recommending his process, was aware of several points which he considered to be sources of error, among which may be mentioned:—

- (I.) The inclusion of alkaline salts not readily removable by washing.
- (II.) Incompleteness of precipitation.
- (III.) The impracticability of converting zinc ammonium phosphate into pyrophosphate without involving loss of zinc.

The first source of error may, as is well known, be to a large extent avoided (completely when weighing as ignited pyrophosphate) by the substitution of ammonium phosphate for the sodium salt, or possibly less completely by the use of microcosmic salt.

With regard to the second objection, that of incompleteness of precipitation, it will be seen, from the test-analyses that follow, that under suitable conditions the amount of zinc in the filtrate does not exceed two- or three-tenths of a m.grm., and is generally less.

The third objection is gone into somewhat more fully later on; but it may be mentioned here that, notwithstanding Tamm's statement, it has since been generally assumed that if care be taken during the ignition no reduction is to be feared.

For the experiments that follow, two sources of zinc to serve as a standard were used, and no difference could be detected in the results yielded by the two specimens.

The first was a purchased sample of chemically pure zinc oxide, 10 grms. of which was carefully tested for impurities with a negative result. The other specimen was obtained as follows:—Excess of pure zinc oxide was left for some days in contact with pure dilute sulphuric acid; after filtration a few drops more acid were added, and sulphuretted hydrogen passed in until a considerable precipitate of white zinc sulphide had appeared. The liquid was then filtered, and a few drops of bromine added, sufficient to produce a faint yellow colour. The solution was now fractionally precipitated with ammonia, the first portion thrown down being rejected. After filtration a portion of the remaining zinc was thrown down as basic carbonate by means of warm ammonium carbonate solution. The precipitate was well washed at the pump, dried, and ignited in a large platinum dish; then again washed with boiling distilled water, and finally ignited over the blowpipe flame in a porcelain crucible. The ignition was invariably repeated immediately before any portion of either of the two specimens was weighed out.

The ammonium phosphate employed contained slightly over 80 per cent of the di-ammonium salt, the remainder being the di hydrogen ammonium phosphate. Its solution was carefully filtered from a trace of insoluble matter. It was perfectly free from arsenic, chlorine, and other common impurities. In all cases, unless otherwise stated, the amount of phosphate employed was equal to ten times the weight of zinc known to be present.

The ammonium chloride was prepared as required by means of pure hydrochloric acid and ammonia.

In all cases precipitation was carried out in platinum vessels, in order to avoid the well-known corrosive action of alkaline phosphate solutions on glass. The bulk of liquid in which precipitation took place was about 150 c.c. The precipitate in all cases was collected on asbestos contained in a Gooch crucible, and well washed with a hot 1 per cent solution of ammonium phosphate. This was considered necessary, as it was found that prolonged contact with hot water tended to bring about partial decomposition of the precipitate, and so lead to low results. The ammonium phosphate solution adhering to the precipitate was removed by a few washings with re-distilled alcohol. The strongest alcohol should not be used for this purpose, as ammonium phosphate is insoluble in it. Cold water may, if preferred, be substituted for the alcohol, but the former has the advantage in that the precipitate dries very much more quickly.

It may here be noticed that, after filtering ammonium phosphate solutions through a filter made of the particular sample of asbestos employed, a slight, though quite perceptible, loss was observed in the weight of the filter, although the asbestos had been thoroughly well purified by treatment with concentrated hydrochloric acid; so that, when exceptional accuracy is required, it is preferable to weigh the crucible and felt after the filtration rather than before. The precipitate should be dissolved in dilute nitric acid, taking care that no fine asbestos fibres are lost, and the crucible and felt dried at 100–105° if the precipitate was weighed as zinc ammonium phosphate, or ignited and weighed in the case of the pyrophosphate. The weight of the crucible and felt, dried at 100–105° C., will invariably be found to be a few tenths of a m.grm. higher than if it had been ignited.

It is obviously of importance to be assured of the complete stability of the zinc ammonium phosphate at the temperature at which it is dried, and, as far as I am aware, no experiments have been given in support of this. The following table is therefore given. (See next column).

The numbers given represent the weight in grammes of the precipitate, dried for the length of time indicated. The numbers in brackets represent the equivalent weights of zinc.

Two specimens of the precipitate, dried for seven and ten hours respectively, both yielded 9.57 per cent of ammonia when distilled with caustic soda, the theoretical amount being 9.56 per cent. So that it may be safely

TABLE I.

Time of drying at 100–105° C.	Expt. I.	Expt. II.	Expt. III.	Expt. IV.
One hour ..	0.3509 (0.1286)	0.5174 (0.1895)	0.7454 (0.2731)	—
Two hours ..	0.3504 (0.1284)	0.5168 (0.1893)	0.7444 (0.2728)	0.3880 (0.1422)
Ten hours ..	0.3504 (0.1284)	0.5167 (0.1893)	0.7444 (0.2728)	0.3880 (0.1422)
Twenty hours	0.3504 (0.1284)	0.5167 (0.1893)	0.7440 (0.2727)	—

assumed, for all practical purposes, that the precipitate is perfectly stable at 100–105° C.

When it was necessary to ignite the precipitate, the Gooch crucible was placed inside a much larger platinum crucible, and heated at first over a very small flame, every care being taken to exclude reducing gases. The lids of the crucibles should be kept off, so as to allow of the free escape of ammonia and water-vapour, as it was found that at high temperatures the ammonia is capable of exerting a reducing action on the precipitate,—possibly due to the partial decomposition of the ammonia into its elements, which begins at 500° C. This reduction was observed by igniting portions of zinc ammonium phosphate precipitate in a porcelain boat, placed inside a porcelain tube which passed through the centre of a Fletcher furnace. At lower temperatures, such as obtain in a tube placed in an ordinary combustion furnace, little or no reduction was observable. After the ammonia and water have been to a large extent expelled, the ignition is completed by replacing the lid and heating more strongly for a short time over a full Bunsen flame. That this degree of heat is amply sufficient was proved by obtaining identical results whether the precipitate be ignited over a Bunsen or blowpipe, or in a muffle at a bright red heat. So that the use of the blowpipe, as has been advocated, is unnecessary. The pyrophosphate should be absolutely white, any greyness—sometimes observable on the surface—indicating more or less reduction.

Various methods of precipitation have been advocated at different times; they may be grouped into three classes:—

- (I.) Tamm's original method, in which a faintly acid solution of zinc ammonium chloride is precipitated by an excess of alkaline phosphate.
- (II.) The acid zinc and phosphate solutions being mixed, the whole is rendered alkaline by the addition of ammonia, the excess of which is expelled by boiling (R. C. Boyd, *School of Mines Quarterly*, xi., p. 355; also L. Jawein, *Chem. Zeit.*, xi., p. 347).
- (III.) Where the alkaline zinc and phosphate solutions are rendered neutral by the cautious addition of acid (Dr. J. Clark, *J. S. C. I.*, 1896, p. 866; also A. C. Langmuir, *Fourn. Amer. Chem. Soc.*, xxi., p. 115).

It will be found that the first original method involves the least trouble, and yields results equally as accurate as those yielded by the other two modifications.

The modified process by which the following results were obtained may be described as follows:—

The acid zinc solution contained in a platinum dish is nearly, but not quite, neutralised by the addition of ammonia, diluted to about 150 c.c., and then warmed on the water-bath. (It is not advisable to heat on a hot plate or sand-bath, as, owing to the very rapidly settling nature of the precipitate, "bumping" is liable to ensue). To the warm solution ammonium phosphate solution is added, in quantity such that ten times the weight of salt is used for 1 part of zinc supposed to be present. The amorphous precipitate first produced quickly changes to a finely crystalline precipitate of zinc ammonium phosphate, the change being especially rapid in presence of considerable amounts of ammonium salts. The

heating is continued for about a quarter of an hour, and then the dish removed and allowed to stand for a short time. No difference could be detected between the results obtained when the liquid was allowed to stand for half an hour or twenty-four hours. The precipitate is next filtered off on a Gooch crucible washed with hot 1 per cent ammonium phosphate solution till perfectly free from chlorides, &c., and then washed a few times with alcohol or cold water. The precipitate is then dried at 100–105° C., and either weighed as Zn, NH₄, PO₄, or ignited, with the previously mentioned precautions, and weighed as Zn₂P₂O₇. The precipitate is then dissolved in dilute nitric acid, the crucible and felt being then weighed, after drying or igniting, under the same conditions as before.

TABLE II.

No.	Zinc taken.	ZnNH ₄ PO ₄ obtained.	=Zn found.	Error.	Ammonium phosphate. Grms.	Ammonium chloride. Grms.	Zinc in filtrate.
1.	0.2856	0.7788	0.2854	-0.0002	2.9	1	trace
2.	0.2000	0.5453	0.1998	-0.0002	2.0	1	0.0003
3.	0.1219	0.3325	0.1218	-0.0001	1.2	1	trace
4.	0.1259	0.3434	0.1258	-0.0001	1.3	1	—
5.	0.2000	0.5461	0.2001	+0.0001	2.0	1	—
6.	0.1029	0.2827	0.1036	+0.0007	1.0	1	0.0001
7.	0.2598	0.7087	0.2597	-0.0001	2.6	1	0.0002
8.	0.1663	0.4531	0.1660	-0.0003	1.7	2	0.0002
9.	0.1727	0.4713	0.1727	—	1.7	2	trace
10.	0.2185	0.5946	0.2179	-0.0006	2.2	2	0.0003
11.	0.1288	0.3504	0.1284	-0.0004	1.3	2	trace
12.	0.2069	0.5653	0.2071	+0.0002	2.0	3	trace
13.	0.2826	0.7715	0.2827	+0.0001	2.8	5	0.0002
14.	0.1426	0.3880	0.1422	-0.0004	1.5	5	—
15.	0.1390	0.3781	0.1385	-0.0005	1.4	5	—
16.	0.1326	0.3603	0.1320	-0.0006	1.3	5	—
17.	0.3512	0.9585	0.3512	—	3.5	5	trace
18.	0.2044	0.5585	0.2047	+0.0003	2.0	7.5	—
19.	0.1935	0.5282	0.1935	—	2.0	10	0.0002
20.	0.1318	0.3598	0.1318	—	1.2	10	—
21.	0.1383	0.3762	0.1379	-0.0004	1.3	10	0.0001
22.	0.1509	0.4098	0.1502	-0.0007	1.5	10	—
23.	0.2000	0.5478	0.2007	+0.0007	2.0	10	—
24.	0.2163	0.5924	0.2171	+0.0008	2.1	15	—
25.	0.1877	0.5165	0.1893	+0.0016	1.8	20	0.0002

TABLE III.

No.	Zinc taken.	Zn ₂ P ₂ O ₇ obtained.	=Zn found.	Error.	Ammonium phosphate. Grms.	Ammonium chloride. Grms.	Zinc in filtrate.
1.	0.1259	0.2925	0.1255	-0.0004	1.3	1	0.0001
2.	0.2000	0.4649	0.1995	-0.0005	2.0	1	trace
3.	0.1428	0.3341	0.1433	+0.0005	1.4	1	—
4.	0.1545	0.3594	0.1542	-0.0003	1.5	1	—
5.	0.2000	0.4674	0.2005	+0.0005	2.0	1	0.0003
6.	0.1029	0.2413	0.1035	+0.0006	1.0	1	0.0001
7.	0.2598	0.6045	0.2594	-0.0004	2.6	1	0.0002
8.	0.2000	0.4637	0.1990	-0.0010	2.0	1	0.0003
9.	0.1219	0.2831	0.1215	-0.0004	1.2	2	trace
10.	0.1663	0.3867	0.1659	-0.0004	1.6	2	0.0002
11.	0.1727	0.4028	0.1728	+0.0001	1.8	2	trace
12.	0.1288	0.2992	0.1284	-0.0004	1.3	2	0.0001
13.	0.1326	0.3077	0.1320	-0.0006	1.3	5	—
14.	0.1390	0.3227	0.1385	-0.0005	1.4	5	—
15.	0.1426	0.3312	0.1421	-0.0005	1.4	5	—
16.	0.2000	0.4672	0.2004	+0.0004	2.0	5	0.0002
17.	0.2190	0.5095	0.2186	-0.0004	1.9	10	trace
18.	0.1353	0.3166	0.1358	+0.0005	1.4	10	trace
19.	0.2330	0.5439	0.2334	+0.0004	2.3	10	trace
20.	0.1935	0.4524	0.1941	+0.0006	2.0	10	0.0002
21.	0.1383	0.3213	0.1379	-0.0004	1.4	10	—
22.	0.1509	0.3498	0.1501	-0.0008	1.5	10	—
23.	0.1318	0.3070	0.1317	-0.0001	1.3	10	—
24.	0.2000	0.4649	0.1995	-0.0005	2.0	10	0.0003
25.	0.2000	0.4662	0.2000	—	2.0	10	0.0002

From the above two tables it will be seen that fairly accurate results may be easily obtained, weighing either as zinc ammonium phosphate or as pyrophosphate.

When the proportion of ammonium chloride is high, 15 or 20 grms. for instance, some difficulty will be found in completely washing the precipitate free from chloride, so that, on dissolving the precipitate in nitric acid, a distinct reaction with silver nitrate will be obtained, as was the case in numbers 24 and 25 in Table II. In such cases weighing as pyrophosphate is to be recommended. In all cases where weighing as the double salt is resorted to, it is as well to be assured of the purity of the precipitate by testing as described. As a rule only the very faintest opalescence will be obtained.

The figures given in the seventh column of the two tables represent the total amount of ammonium chloride present after the completion of the reaction,—i. e., the total chlorine calculated as NH_4Cl .

In the extreme right hand column is found the amounts of zinc left in the filtrates. This was detected, and in some cases estimated as follows:—The clear filtrate, after concentration if necessary, was made strongly alkaline with ammonia, then a few drops of ammonium sulphide added, and the whole kept in a warm place for at least twenty-four hours. One-tenth of a m.grm. of zinc gives a perceptible precipitate, in solutions containing ammonium chloride and phosphate, when treated in this way. An attempt to estimate these small amounts was made in the following way:—The liquid was filtered through a Swedish filter-paper, and washed as rapidly as possible, with a little cold distilled water, using the pump to hasten the filtration and so reduce risk of oxidation. The filter-paper with the trace of zinc sulphide on it is then returned to the flask in which the precipitation was effected (taking care to expel by blowing any sulphide vapours from the flask), and an excess of standardised approximately N/100 iodine solution added, together with a drop or two of very dilute hydrochloric acid. After a short time the excess of iodine is titrated back with N/100 sodium thiosulphate. Both volumetric solutions were standardised each time they were used. A similar process, applicable to larger amounts, has quite recently been published by Pouget (*Comptes Rendus*, cxxix., 45—47). No great accuracy is claimed for the figures thus obtained; they are merely intended to approximately indicate the error involved. Where no entry is made as to the amount of zinc in the filtrate, it may be taken as being less than one-tenth of a m.grm., and therefore too small to estimate.

The next point investigated was as to whether the process was equally applicable to sulphates and nitrates.

The following results (Table IV.) clearly indicate that they exert no disturbing influence.

TABLE IV.

No.	Zinc taken.	Zinc found as ZnNH_4PO_4 .	Error.	Zinc found as $\text{Zn}_2\text{P}_2\text{O}_7$.	Error.	Ammonium salts, Grms.	Zinc in filtrate.
NH_4NO_3 .							
1.	0.1544	0.1553	+0.0009	0.1553	+0.0009	1	0.0001
2.	0.1109	0.1107	-0.0002	0.1106	-0.0003	2	0.0002
3.	0.1106	0.1100	-0.0006	0.1100	-0.0006	5	—
4.	0.0922	0.0919	-0.0003	0.0919	-0.0003	10	—
$(\text{NH}_4)_2\text{SO}_4$.							
5.	0.1732	0.1731	-0.0001	0.1729	-0.0003	0.75	0.0002
6.	0.1295	0.1295	—	0.1296	+0.0001	1.5	trace
7.	0.1112	0.1108	-0.0004	0.1108	-0.0004	5	—
8.	0.1358	0.1351	-0.0007	0.1351	-0.0007	10	—

In the above table the results obtained by weighing, both as ZnNH_4PO_4 and as $\text{Zn}_2\text{P}_2\text{O}_7$, are given, and the almost absolute coincidence of the figures obtained by the two methods should be noticed, the extreme difference being two-tenths of a m.grm.

Since, as before stated, it has been considered proved that, under slightly different conditions to those obtaining

in the method described, unless a large amount of ammonium chloride is present in the zinc solution, the precipitate thrown down by an alkaline phosphate does not strictly correspond to the formula ZnNH_4PO_4 , it seemed desirable that other confirmation than test-analyses should be given of the correctness of composition of the precipitate thrown down in the preceding modification. Accordingly the following analyses are given (Table V.) of precipitates obtained from zinc chloride solutions containing varying percentages of ammonium chloride. The precipitates were prepared and treated in exactly the same way as in an actual analysis.

TABLE V.

	ZnNH_4PO_4 from NH_4Cl solution.			ZnNH_4PO_4 from NH_4Cl solution.			ZnNH_4PO_4 from NH_4Cl solution.		
	Theory.	1 per cent	Diff.	5 per cent	Diff.	10 per cent	Diff.		
ZnO ..	45.60	45.55	-0.05	45.62	+0.02	45.48	-0.12		
NH ₃ ..	9.56	9.57	+0.01	9.58	+0.02	9.50	-0.06		
H ₂ O ..	5.05	5.09	+0.04	5.05	—	5.13	+0.08		
P ₂ O ₅ ..	39.79	39.79	—	39.75	-0.04	39.89	+0.10		
	100.00	100.00		100.00		100.00			

The ZnO was determined by observing the weight of precipitate yielded by a known weight of pure zinc oxide. The ammonia was determined by the distillation of about 2 grms. of the precipitate with excess of caustic soda, the evolved NH_3 being absorbed in standard acid, the excess of which was determined by titration in the ordinary way.

The water was determined by subtracting the figure found for the ammonia from the total loss on ignition. The phosphoric acid was taken by difference.

It will be seen that the numbers obtained agree satisfactorily with theory, so that it may be safely assumed that the precipitate is of correct constant composition whether much or little ammonium chloride be present.

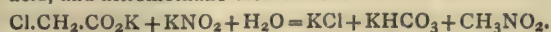
It may be of interest to note that an unsuccessful attempt was made to apply Stolba's alkalimetric method for the titration of magnesium ammonium phosphate to the zinc salt. It was also noticed that, if ammonium arsenate be substituted for the phosphate, an uninviting gelatinous precipitate is obtained, quite unlike the double phosphate. The filtrate contained traces of zinc. It was not further investigated.

It is my intention to apply the preceding modification to the estimation of other metals, especially manganese, since Gooch and Austin (*Amer. Journ. Sci.*, 1898, vi., 223) consider that, under ordinary conditions, large amounts of ammonium salts are needed if accurate results are to be obtained.

In conclusion, I wish to express my thanks to Professor Smithells for advice and help in connection with the above paper.—*Zeitschrift f. Anal. Chemie*, xxxix., 273—284.

The Yorkshire College, Leeds.

New Method for the Preparation of the Nitromethanes.—V. Auger.—When we react with chloroacetate of potassium on nitrite of potassium in concentrated aqueous solution, a lively reaction is produced on heating the mixture, with the disengagement of carbonic acid, and nitromethane distils over:—



Wishing to see if this isolated reaction was susceptible of generalisation, the author first applied it to the α -bromine derivatives of the acids of the fatty series, and obtained the best results by operating as quickly as possible with the dry materials, and slightly overheating the flask, to prevent the product formed from falling back.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 9.

SYNTHETIC INDIGO.*

By EDWARD S. JOHNSON.

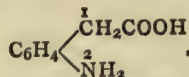
(Continued from p. 90).

I. THE SYNTHESIS OF INDIGO.

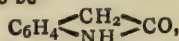
THE wonderful investigations of Baeyer and his pupils, which almost exclusively underlie this development, are so remarkable as examples of consistently prosecuted, perspicuous, resourceful, and prolific research, and withal so absolutely essential to a discussion of synthetic indigo, that they will throughout be reviewed somewhat in detail. To this will be added a brief consideration of the chief of more recent technically important syntheses.

1. Baeyer's Syntheses.

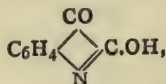
The first of these most interesting formative processes is based upon *o*-amidophenylacetic acid (Baeyer, "Synthese d. Isatins u. d. Indigblaues," *Ber. Deut. Chem. Gesell.*, xi, 1228),—



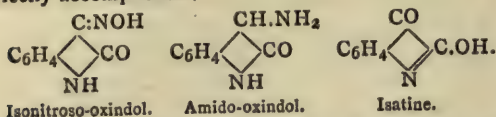
The anhydride of the acid was shown by Baeyer "Synthese d. Oxindols," *Ber. Deut. Chem. Gesell.*, xi, 584) to be identical with oxindol, one of the compounds of the indigo-group then already known, and in the investigation referred to shown to be—



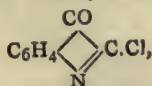
the anhydride of *o*-amidophenylacetic acid. The preparation of isatine,—



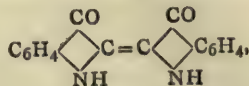
had already been long before realised by the work of Baeyer and Emmerling (*Ber. Deut. Chem. Gesell.*, iii, 514) by the action of phosphorus, phosphorus dichloride, and acetyl chloride upon that substance. The problem therefore consisted in substituting H_2 in the methylene group, CH_2 , of oxindol by oxygen. Great difficulty was experienced in effecting the change, being found impossible by direct oxidation. With the idea of facilitating the desired reaction, chlorine, bromine, &c., were substituted in the methylene group, but all unsuccessfully; by means of nitrous acid, and thus the introduction of the isonitro-group NOH , and reduction, the oxidation was readily and perfectly accomplished:—



The slight yield by the old process for bringing about the last stage of the operation was later (*Ber. Deut. Chem. Gesell.*, xi, 1296; and xii., 456) improved, and the nature of the reaction more fully explained by the use of phosphorus pentachloride. Hereby isatine chloride,—

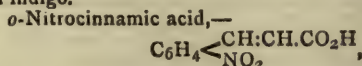


is formed and by reduction (P , $\text{Zn} + \text{HCl}$, &c. transformed into indigo,—

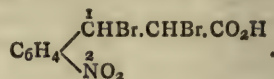


"Thereby for the first time a synthesis of indigo from coal-tar has been effected" (*Ber. Deut. Chem. Gesell.*, xi, 1228). It dates from the year 1878.

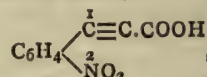
Following shortly, in 1880, upon the *o*-amidophenyl-acid synthesis, came the famous investigations starting with *o*-nitrocinnamic acid. They brought to light a series of most peculiar and astonishing substances, the study of which in the main definitely made plain the constitution of indigo.



by addition of bromine is converted into *o*-nitroindibrom-cinnamic acid,—

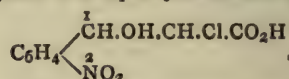


By alkali in the cold, the bromine may be removed in the form of alkali bromide, leaving—

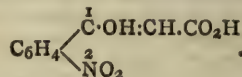


o-nitrophenylpropionic acid. This, with dilute alkali and mild reducing agents, such as milk-sugar, grape-sugar, and xanthates, produces indigo.

With hypochlorites in alkaline solution, *o*-nitrocinnamic acid further yields *o*-nitrophenylchloroacetic acid,—



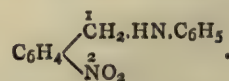
Alcoholic solution of alkali extracts one molecule of hydrochloric acid and *o*-nitrophenyloxacrylic acid,—



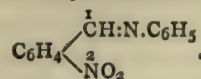
results. Heating at 100° in the presence of a solvent, such as acetic acid or phenol, completes the conversion into indigo. The yield of the latter form of the *o*-nitrocinnamic acid process is slight, while the first mentioned amounts to 70 per cent of the theoretical (Reissert, "Indigo-synthesen," 7).

Baeyer and Drewsen in 1882 published the discovery by them of the formation of indigo from *o*-nitrobenzaldehyde and acetone. This, at that time unaccountable, process was fully investigated by its discoverers. By it indigo is formed when a mixture of the aldehyde and acetone, acetaldehyde, or phenylglyoxalic acid is warmed in the presence of alkali.

The technical starting-point for the preparation of indigo by this method is toluene; this hydrocarbon is nitrated, producing as a main product the *o*-nitro-derivative. This is chlorinated in the methyl-group—a reaction which is only possible to the extent of about 50 per cent without introducing chlorine into the benzene ring also. The separating of the *o*-nitrobenzylchloride formed, from unaffected nitrotoluene, is accomplished by the action of aniline upon the mixture, producing *o*-nitrobenzyl-aniline,—



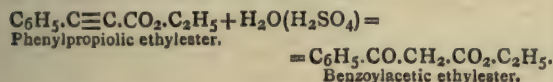
By oxidation, *o*-nitrobenzylideneaniline is formed,—



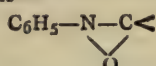
Boiling with hydrochloric acid converts the substance into the aldehyde sought and aniline hydrochloride.

* Proceedings of Engineers' Society of Western Pennsylvania, xvi., No. 3.

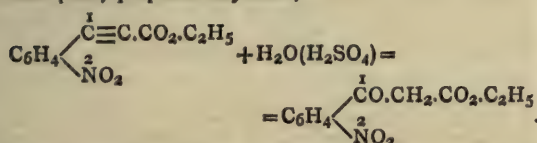
The transformations involved in the conversion of *o*-nitrophenylpropionic acid into indigo are of somewhat complicated nature. Their explanation is based upon certain experimentally derived facts, and assumptions from analogy. Baeyer (*Ber.*, xv., 2705; further, in same connection, compare Reissert, "Indigosynthesen," 19-23, and the literature there referred to) observed that phenylpropionic ethylester by the action of slightly diluted sulphuric acid is converted into benzoylacetic ester,—



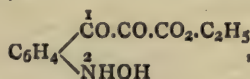
It is also a general observation that nitro-groups united to the benzene ring are deprived partially or even wholly, without the use of reducing agents, of oxygen by mobile (easily oxidisable) hydrogen atoms held by carbon attached to the benzene ring in *o*-position to the nitro-group. Moreover, it is known that carbonyl groups (=CO) of aldehyde or ketone nature react with phenylhydroxylamine, cause water to separate, and form compounds which contain the combination of atoms—



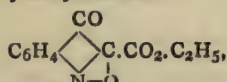
With these facts in mind, analogous transformations may be readily recognised as possible in the case of *o*-nitrophenylpropionic ethylester,—



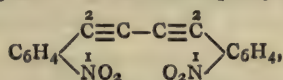
In the *o*-nitrobenzoylacetic ethylester thus formed, intramolecular reduction produces *o*-hydroxylaminobenzoyloxalic ethylester,—



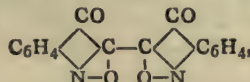
which becomes by anhydriation—



isatogenic ethylester. As to dinitrodiphenyldiacetylene,—

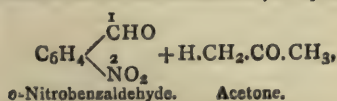


which contains the characteristic group of *o*-nitrophenylpropionic acid twice, it is at once seen how di-isatogen,—

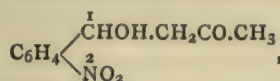


may be derived. By comparison of its formula with that of indigo, it is apparent that the latter is produced by the removal from di-isatogen of two atoms of oxygen and the addition of two atoms of hydrogen; in other words, by reduction. This relationship is in perfect accord with the actual observation.

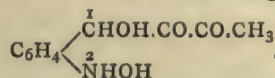
In the case of the *o*-nitrobenzaldehyde synthesis,—



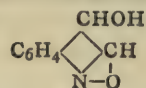
o-nitrophenyllactic ketone,—



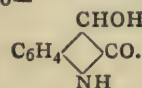
is formed as a first phase of the reaction, and is transformed, by internal reduction of the nitro-group, to—



The alkali added to the original mixture separates acetyl (—CO·CH₃) as acetate. This and anhydriation produce—



which may be conceived as changing, by the migration of an hydrogen atom, to—

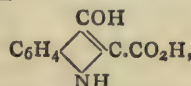


The splitting off of two molecules of water from two molecules of such a combination would result in the formation of indigo.

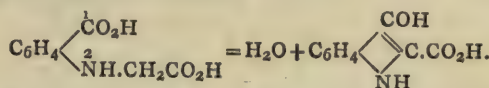
With the last-named synthesis, the following shares the greatest technical importance (Friedlaender, "Fortschritte d. Theerfarbenfabrikation," iv., 1027); it is the—

2. Heumann Synthesis.

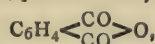
In its most recent form, it consists in the preparation of *indoxyl acid*,—



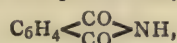
which is readily converted into indigo by alkaline fusion of phenylglycine-*o*-carboxylic acid:—



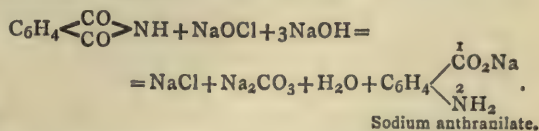
The original raw material for the process is naphthalene, from which, by the action of concentrated sulphuric acid at high temperatures, phthalic anhydride,—



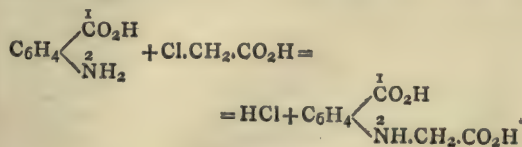
is obtained. From this, phthalimide,—



is prepared by means of ammonia gas. Phthalimide in alkaline solution is converted by sodium hypochlorite into anthranilic acid:—



With monochloroacetic acid, phenylglycine-*o*-carboxylic acid is formed:—



(To be continued).

NOTICES OF BOOKS.

Twenty-fourth Annual Report of Her Majesty's Inspectors of Explosives; being their Report for the Year 1899. London: Darling and Sons. 1900. Pp. 190.

THE department has sustained a loss in the retirement of Colonel Ford, C.B., who succeeded to the post of Chief Inspector on the death of Sir Vivian Majendie. Colonel Ford reached the age limit on the 15th of August, 1899, and was obliged to retire on that date according to the regulations. He is succeeded by Captain J. H. Thomson.

The only modification of the law made during the past year has been an amendment of Order of Secretary of State, No. 3, in regard to the packing of cordite for Government contract.

The growth of trade in explosives during the past year is shown by the great increase in the number of factories, and also by the increased activity in many of the leading factories. The Inspectors, we are glad to see, are able to report that the condition and management of the various factories and magazines visited by them are, in the majority of cases, excellent, and that there has been no falling off in the high standard previously attained, but we may be permitted to ask why the management should not by now be excellent in *all* cases?

The number of deaths (three) from accidents by fire or explosion in manufacture this year is again below the average for the decade (4.4).

The total number of factories under continuing certificate or license is 151. The total number of factories which have come into existence since the commencement of the Act is 140, but 44 factories have become extinct. The net increase is therefore 96; the net increase for the present year is eight.

The additions to the list of authorised explosives number fifteen, there is one alteration of name, five additions to the authorised list, and seven alterations in definitions.

The character of the samples taken for examination during the year has been satisfactory, Dr. Dupré's report (Table I.) showing that of 303 samples examined by him only 13 were rejected.

During the year the Inspectors have paid 214 visits to factories, now numbering 151, so that every one has been visited at least once, and nearly half of them a second time. Only one case has occurred during the year in which the Inspector's visit necessitated recourse to judicial proceedings.

The number of accidents reported during the year is 54, causing three deaths and injuring 24 persons. Eight cases of illegal manufacture have come to the Inspector's notice during the year.

There is a considerable falling off in the quantity of nitroglycerin compounds imported during the year, the amount being 798,350 lbs., against 983,000 lbs. in 1898; the amount of non-nitroglycerin explosives imported has also fallen from 177,100 lbs. to 140,882 lbs.

The year has again been one of considerable activity among inventors, and as many as thirteen new explosives have been submitted for examination, or had been left over from the preceding year. The chief point of interest connected with this part of the subject is the fact that for the first time for many years a chlorate mixture has passed successfully through all the tests.

Among the miscellaneous accidents, not immediately connected with blasting, it is significant to notice that the largest number come under the head of "Playing with Detonators," the number having increased from 15 to 22 since the previous year. Of these five occurred to grown up persons, the remainder, however, occurred with detonators which had got into the hands of children. In their last report the Inspectors suggested means by which these accidents could be diminished, and since then rules have been inserted in the Explosives in Coal Mines Order

of July 24th, by which detonators are to be issued only to shot-firers, and to be safely kept by them. These rules only came into force in October last, and it is perhaps too soon to judge of their effect. If, however, the number of such accidents does not decrease during the current year, the Inspectors consider that the alternative suggestion in their last report, viz., that of rendering the detonators less attractive in appearance, should be tried. It is true that these accidents seldom cause loss of life, but it should be remembered that the children who lose fingers or a hand from these explosions are thereby handicapped in the struggle for existence, which in this country is becoming yearly more and more severe.

First Stage Hygiene. By ROBERT A. LYSTER, B.Sc., Lond. London: W. B. Clive, University Tutorial Press. 1900. Pp. 199.

THE increased popularity of the study of hygiene and public health is one of the chief reasons that have led to the publication of this work, and the author believes that it embodies the first attempt that has been made to treat the successive points in logical order. Chapter I. deals with the general build of the body; this is followed by chapters on the blood, air, respiration, ventilation, and foods. In Chapters VI. to X. we have to do with the digestive system, examples of foods, cooking, beverages, &c. There is an interesting chapter, No. XVII., on water supply, in which the general composition and the commoner impurities of water are given, with simple methods for their detection. There is also a useful chapter on accidents and emergencies (No. XV.), describing the best steps to take in cases of cuts, sprains, drowning, suffocation, burns, hysteria, poisoning, &c.

At the ends of those chapters in which the subject matter adapts itself to such treatment, a list of simple experiments, illustrating the work covered by the chapter, has been added. The performance of these experiments will be very useful in helping to fix the facts in the student's memory.

Elementary Practical Chemistry for Schools of Science.

By THOMAS CARTWRIGHT, B.A., B.Sc., Lond. London, Edinburgh, and New York: Thomas Nelson and Sons. 1900. Pp. 140.

IN this volume the author has attempted to strike the happy mean between the method of discovery and the method of telling, believing that those who would abolish telling and insist on the learner being entirely a discoverer, are as much in the wrong as the teacher who puts his faith in the lecture-room rather than in the laboratory.

The author begins with measuring and weighing, simple blowpipe work, &c., then goes on to experiments with sand and saltpetre, illustrating the operation of separation by means of solution, filtration, and recovery by evaporation. These are followed by experiments with air, oxygen, water, acids, chalk, sulphur, &c., with a few volumetric exercises, and a short chapter on chemical theory.

The book is well arranged and clearly written, and should be found useful by teachers of science for beginners.

Note on Chloronaphthylamine, $C_{10}H_6ClNH_2$ 1.4.—F. Reverdin and P. Crépieux.—On attempting to prepare dichloronaphthylamine by the chlorisation of acetyl-naphthylamine, by means of chlorate of soda and hydrochloric acid, the authors obtained a base after saponification, which, when distilled with steam and crystallised several times in ligroin, fused at 98°, while its acetyl derivative had the fusing-point 186.5°. Analysis showed that this base is a monochloronaphthylamine.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 9.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 5, July 30, 1900.

Electrolysis of Concentrated Solutions of Hypochlorites.—André Brochet.—The author's experiments show that the electrolysis of a hypochlorite proceeds in the same way as a chloride, and tends towards the same limits.

Gadolinium.—Eug. Demarçay.—(See p. 97).

Diphenylcarbazide as a very Sensitive Reaction for some Metallic Compounds.—P. Cazeneuve.—Diphenylcarbazide, as the author previously showed, is transformed into diphenylcarbazone by losing two atoms of hydrogen under the influence of certain oxides and metallic salts. During this reaction, the diphenylcarbazone formed combined with the metal gives characteristic colours. Salts of copper, mercury, and particularly the per-salts of iron, act in the cold in aqueous solution, forming cuprous, mercurous, and ferrous derivatives of a decidedly intense colour, allowing of the detection of the metal in solutions containing 1/100,000th part of the metallic salt. The diphenylcarbazide, when used as a reagent, should be pure and white; this can be obtained by crystallisation from concentrated acetic acid or pure acetone, and drying the compound at 60°. Copper salts impart a violet colour, mercury a pale blue tint, and iron a peach flower colour, which becomes a dull brown on agitation with ferrocyanide. These colourations are much more sensitive than the ordinary reactions, but they are destroyed by mineral acids and organic acids in excess.

No. 6, August 6, 1900.

Boiling-points of Zinc and Cadmium.—Daniel Berthelot.—The author used specimens of extremely pure zinc, obtained from M. Férent, in which the proportion of impurity was less than one-thousandth part of the whole. Four experiments gave the numbers 924°, 913°, 914°, 922° as the boiling-points of zinc, the mean of these determinations being 920°. A pure specimen of cadmium, also obtained from M. Férent, gave coincident results for three experiments, the boiling-point being 778°.

Atomic Weight of Radio-active Barium.—Mdme. Curie.—(See p. 98).

Electrolytic Estimation of Cadmium.—Dmitry Balachowsky.—The author obtained, by electrolysis of solutions of bismuth and cadmium, metallic precipitates absolutely free from oxide, very adherent, and easy to wash. The difference in the conditions of precipitation of these two bodies, led the author to devise a means of separation of these two elements which will form the subject of a future paper. He also confirmed the fact that the electrolytic method constitutes an excellent way of obtaining bismuth in a state of absolute purity, as previously shown by A. Classen.

Some New Spectra of Rare Earths.—Eug. Demarçay.—Will be inserted in full.

Blue Oxide of Molybdenum.—Marcel Guichard.—The author succeeds in isolating the blue hydrated oxide of molybdenum in a state of purity. He describes the conditions which are necessary to obtain easily a considerable quantity. His analyses appear to show that it has the formula $\text{MoO}_2 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$. A further investigation of this compound is being made, which will form the subject of a future paper.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 9.

A Regulating Furnace for Fixed Temperatures.—A. Gautier.—Already noticed.

Thermic Study of Protocatechic or Dioxibenzoic Acid. Influence of the Phenolic Oxhydriles.—G. Massol.—Commercial protocatechic acid is very impure; the author purified it by fractional crystallisation, transformation into the potash salt, decolouration by bone-black, decomposition of the salt by sulphuric acid, solution of the acid in ether, and fresh crystallisation: it then occurs in beautiful bright yellow, prismatic needles, fusible at 199°. The acidimetric assay made with a normal solution of soda, and without any added indicator, gave a first golden-yellow indication a little before the addition of 1 molecule of alkali (0.88 to 0.90 mol.), then the solution gradually became darker, each drop of alkali produced a rose colouration, and a second wine-red indication was distinctly produced by the second molecule of alkali. On adding phenolphthalein, we first noticed the golden-yellow indication, then the phenolphthalein became red on the addition of 1.5 mols. of the base. With litmus the indication takes place with 2 mols. of alkali. These different reactions show the influence of the phenolic oxhydriles on the general acidity of the molecule; it is also observed that the heats of neutralisation are sensibly lower than those given by the meta- and para-oxybenzoic acids, which contain 1 mol. less of oxhydrile. The author has previously concluded, from his experiments on the oxybenzoic acids, that oxhydrile in the ortho-position (salicylic acid) increases the acidity of benzoic acid, while in the meta- and para-positions it has only a feeble influence (about 0.4 cal.), which should enable us to fix the position of the oxhydrile with regard to the carboxyl. These results are applicable to the dioxibenzoic acids: in protocatechic acid the two oxhydriles are in meta- and para-positions, and their total influence on the carboxyl only increases the heat of formation of the salt by 0.29 cal., while it should have been 2 cal. if one of the phenolic oxhydriles had occupied the ortho-position.

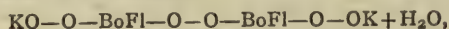
On the Oxide of Diphenylmethanol.—V. Auger.—A controversial paper in which the author concludes that the ether oxide of benzhydrol should keep the formula attributed to it by Linnemann, Zagumeni, Friedel, and Balsohn.

MISCELLANEOUS.

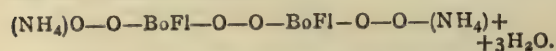
Researches on Graphite.—L. Staudenmaier.—**Graphitic Acid** (from Ceylon graphite).—Crystalline graphitic acid, so-called, is in reality amorphous, and represents a pseudomorphose of crystals of the graphite from which it has been prepared. Chloride of tin transforms it into a brilliant black product, keeping the same crystalline form as the acid, and consequently, of the original graphite. This compound is infusible, only slightly combustible, and resembles graphite entirely. **The Pyro- and Pseudo-graphitic Acids.**—A mixture of 250 c.c. SO_4H_2 and 100 c.c. of water attacks graphitic acid at about 160, giving off CO_2 , and furnishing a brilliant black product, which is pseudomorphic of graphite, very slightly combustible, and easily attacked by oxidising agents; the author calls it pyrographitic acid, although it in no way resembles the product commonly known by this name. It is attacked by nitric acid, giving a series of amorphous red products, and at the same time mellitic acid. Chloric acid attacks it, giving oxidised products, first green, then yellow, resembling graphitic acid, and

its immediate product of combustion, and called by the author pseudo-graphitic acids. These compounds are easily attacked by oxidising agents; they give, with stannous chloride, black products of combustion. The author concludes from his researches that a series of black carbonaceous bodies exists having the appearance of graphite, and a series of green and yellow bodies having the appearance of the graphitic acids. He thinks that graphitic and pseudographitic acids are very complex compounds with a quinonic function, and having carboxylised groups, and that as the complex molecule is attacked the number of these last groups augments at the expense of several quinonic bonds. He is also of the opinion that the study of the graphitic acids can be carried out more easily starting from products with an already simplified molecule similar to that of mellitic acid.—*Berichte*, vol. xxxii., p. 2825.

Fluohyperborates.—P. Melkoff and S. Lordkipanidze. —In a preceding paper the authors have shown that potassic fluoroborate, under the influence of peroxide of hydrogen, is converted into a compound corresponding to the empirical formula $\text{Bo}_4\text{K}_4\text{Fl}_4\text{O}_{11}$. By dissolving this salt in an excess of peroxide of hydrogen, and treating the solution obtained with alcohol, we observe the formation of a viscous precipitate which rapidly changes into a crystalline powder. This latter is soluble in water, and gives off an abundance of oxygen under the action of heat. The new salt, the constitution of which may be expressed by the formula—



ought to be regarded as a fluohyperboric acid, of which the atom of hydrogen has been replaced by the remaining KO. The ammoniacal salt, answering to the formula $(\text{NH}_4)_2\text{Bo}_2\text{Fl}_2\text{O}_6+3\text{H}_2\text{O}$, is obtained by causing equivalent quantities of boric acid and fluoride of ammonium to react in aqueous solution. The solution is treated with an excess of peroxide of hydrogen, and then with ammonia and alcohol. This latter precipitates a fairly stable white crystalline mass, which, in the dry state, gives off a smell of ammonia. Under the influence of heat the aqueous solution of the salt decomposes with the evolution of oxygen and the formation of nitrite of ammonia. From the proportions of boron, ammonia, and active oxygen present in the salt, it is necessary to give it the empirical composition $(\text{NH}_4)_2\text{Bo}_2\text{Fl}_2\text{O}_6+3\text{H}_2\text{O}$ and the extended formula—



As perboric acid has not the property of giving saline compounds with the metallic superoxides, these latter are substituted very easily for the hydrogen atom of fluohyperboric acid.—*Berichte*, vol. xxxii., p. 3510.

A New Method for the Separation of Chlorine and Iodine.—L. Vanino and O. Hauser.—In a previous publication one of the authors has shown that, when we submit halogen derivatives of silver to the influence of alkaline solutions of formic aldehyde, the resistance to reduction increases very rapidly from the chloride to the iodide. On this phenomenon he bases a method for the separation of chlorine from iodine, and he gives the following details of the operations:—The haloid salts are precipitated by means of nitrate of silver, filtered by decantation, and washed with boiling water, taking the necessary precautions to avoid carrying over the least trace of any solid substance. When the washing is complete, the precipitate is treated with 25 c.c. of a solution of 50 grms. of carbonate of potassium in 100 grms. of water and 5 c.c. of 42 per cent formic aldehyde. This is left to stand for some time at the ordinary temperature, and then heated to 30–40° for half-an-hour. As for the particles adhering to the filter, which may have been accidentally carried over during the decantation, they are

also moistened with a few c.c. of the warm mixture of alkaline carbonate and formic aldehyde. Thanks to this treatment, the chloride of silver is converted into metallic silver, while the iodide of silver is not changed. The liquid is again separated by decantation, and the solid portion which remains at the bottom of the beaker is taken up with warm nitric acid. If we then filter again we separate the insoluble iodide of silver from the metallic silver resulting from the reduction of the chloride, and which goes into solution in the dilute nitric acid. There now only remains to weigh the iodide remaining on the filter, and to precipitate the silver contained in the filtrate by means of hydrochloric acid. The author has made a series of estimations, of which the following are two examples:—

		Grm.		Calculated.	Found.
I.	KI	0.2026	AgI	0.2865	0.2866
	KCl	0.1074	AgCl	0.2064	0.2051
II.	KI	0.1425	AgI	0.2015	0.2004
	KCl	0.0988	AgCl	0.1899	0.1892

—*Berichte*, vol. xxxii., p. 3515.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

White Rubber.—Can any correspondent oblige by informing me whether there is any preparation of white rubber that will stand heat and boiling, and which can be used in the manufacture of small articles that would have to go through these processes?—**RUBBER.**

PATENTS, DESIGNS, AND TRADE MARKS ACTS. 1883 TO 1888.

NOTICE IS HEREBY GIVEN that THE CASTNER-KELLNER ALKALI COMPANY, LIMITED, of 13, Abchurch Lane, in the City of London, have applied for leave to amend the Specification and Drawings of Letters Patent No. 20259 of 1894, granted to Carl Kellner for "Improvements in Electrolytic Apparatus for Decomposing Metallic Salts."

Particulars of the proposed Amendment were set forth in the "Illustrated Official Journal" (Patents) issued on the 22nd of August, 1900.

Any person, or persons, may give notice of opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

(Signed),
C. N. DALTON,
Comptroller-General.

PHILIP M. JUSTICE,
55 & 56, Chancery Lane, London,
Chartered Patent Agent,
For the Applicant.

NOTICE.

The **STUDENTS' NUMBER** of the **CHEMICAL NEWS** will be published on Friday, September 21st. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, 19th September.

THE CHEMICAL NEWS.

VOL. LXXXII., No. 2128.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BRADFORD, 1900.

INAUGURAL ADDRESS OF THE PRESIDENT,
PROF. SIR WILLIAM TURNER, M.B., D.C.L., LL.D., D.Sc.,
F.R.S.

TWENTY-SEVEN years ago the British Association met in Bradford, not at that time raised to the dignity of a City. The meeting was very successful, and was attended by about 2000 persons—a forecast, let us hope, of what we may expect at the present assembly. A distinguished chemist, Professor A. W. Williamson, presided. On this occasion the Association has selected for the presidential chair one whose attention has been given to the study of an important department of biological science. His claim to occupy, however unworthily, the distinguished position in which he has been placed, rests, doubtless, on the fact that, in the midst of the engrossing duties devolving on a teacher in a great University and School of Medicine, he has endeavoured to contribute to the sum of knowledge of the science which he professes. It is a matter of satisfaction to feel that the success of a meeting of this kind does not rest upon the shoulders of the occupant of the presidential chair, but is due to the eminence and active co-operation of the men of science who either preside over or engage in the work of the nine or ten sections into which the Association is divided, and to the energy and ability for organisation displayed by the local Secretaries and Committees. The programme prepared by the general and local officers of the Association shows that no efforts have been spared to provide an ample bill of fare, both in its scientific and social aspects. Members and Associates will, I feel sure, take away from the Bradford Meeting as pleasant memories as did our colleagues of the corresponding Association Française, when, in friendly collaboration at Dover last year, they testified to the common citizenship of the Universal Republic of Science. As befits a leading centre of industry in the great county of York, the applications of science to the industrial arts and to agriculture will form subjects of discussion in the papers to be read at the meeting.

Since the Association was at Dover a year ago, two of its former Presidents have joined the majority. The Duke of Argyll presided at the meeting in Glasgow so far back as 1855. Throughout his long and energetic life he proved himself to be an eloquent and earnest speaker, one who gave to the consideration of public affairs a mind of singular independence, and a thinker and writer in a wide range of human knowledge. Sir J. Wm. Dawson was President at the meeting in Birmingham in 1886. Born in Nova Scotia in 1820, he devoted himself to the study of the Geology of Canada, and became the leading authority on the subject. He took also an active and influential part in promoting the spread of scientific education in the Dominion, and for a number of years he was Principal and Vice-Chancellor of the McGill University, Montreal.

Scientific Method.

Edward Gibbon has told us that diligence and accuracy are the only merits which an historical writer can ascribe

to himself. Without doubt they are fundamental qualities necessary for historical research, but in order to bear fruit they require to be exercised by one whose mental qualities are such as to enable him to analyse the data brought together by his diligence, to discriminate between the false and the true, to possess an insight into the complex motives that determine human action, to be able to recognise those facts and incidents which had exercised either a primary or only a secondary influence on the affairs of nations, or on the thoughts and doings of the person whose character he is depicting.

In scientific research, also, diligence and accuracy are fundamental qualities. By their application new facts are discovered and tabulated, their order of succession is ascertained, and a wider and more intimate knowledge of the processes of nature is acquired. But to decide on their true significance a well-balanced mind and the exercise of prolonged thought and reflection are needed. William Harvey, the father of exact research in physiology, in his memorable work "*De Motu Cordis et Sanguinis*," published more than two centuries ago, tells us of the great and daily diligence which he exercised in the course of his investigations, and the numerous observations and experiments which he collated. At the same time he refers repeatedly to his cogitations and reflections on the meaning of what he had observed, without which the complicated movements of the heart could not have been analysed, their significance determined, and the circulation of the blood in a continuous stream definitely established. Early in the present century, Carl Ernst von Baer, the father of embryological research, showed the importance which he attached to the combination of observation with meditation by placing side by side, on the title-page of his famous treatise "*Ueber Entwicklungsgeschichte der Thiere*" (1828), the words "*Beobachtung und Reflexion*."

Though I have drawn from biological science my illustrations of the need of this combination, it must not be inferred that it applies exclusively to one branch of scientific inquiry; the conjunction influences and determines progress in all the sciences, and when associated with a sufficient touch of imagination, when the power of seeing is conjoined with the faculty of foreseeing, of projecting the mind into the future, we may expect something more than the discovery of isolated facts; their co-ordination and the enunciation of new principles and laws will necessarily follow.

Scientific method consists, therefore, in close observation, frequently repeated so as to eliminate the possibility of erroneous seeing; in experiments checked and controlled in every direction in which fallacies might arise; in continuous reflection on the appearances and phenomena observed, and in logically reasoning out their meaning and the conclusions to be drawn from them. Were the method followed out in its integrity by all who are engaged in scientific investigations, the time and labour expended in correcting errors committed by ourselves or by other observers and experimentalists would be saved, and the volumes devoted annually to scientific literature would be materially diminished in size. Were it applied, as far as the conditions of life admit, to the conduct and management of human affairs, we should not require to be told, when critical periods in our welfare as a nation arise, that we shall muddle through somehow. Recent experience has taught us that wise discretion and careful provision are as necessary in the direction of public affairs as in the pursuit of science, and in both instances, when properly exercised, they enable us to reach with comparative certainty the goal which we strive to attain.

Improvements in Means of Observation.

Whilst certain principles of research are common to all the sciences, each great division requires for its investigation specialised arrangements to insure its progress. Nothing contributes so much to the advancement of

knowledge as improvements in the means of observation, either by the discovery of new adjuncts to research or by a fresh adaptation of old methods. In the industrial arts, the introduction of a new kind of raw material, the recognition that a mixture or blending is often more serviceable than when the substances employed are uncombined, the discovery of new processes of treating the articles used in manufactures, the invention of improved machinery, all lead to the expansion of trade, to the occupation of the people, and to the development of great industrial centres. In science, also, the invention and employment of new and more precise instruments and appliances enable us to appreciate more clearly the significance of facts and phenomena which were previously obscure, and to penetrate more deeply into the mysteries of nature. They mark fresh departures in the history of science, and provide a firm base of support from which a continuous advance may be made and fresh conceptions of nature can be evolved.

It is not my intention, even had I possessed the requisite knowledge, to undertake so arduous a task as to review the progress which has recently been made in the great body of sciences which lie within the domain of the British Association. As my occupation in life has required me to give attention to the science which deals with the structure and organisation of the bodies of man and animals—a science which either includes within its scope or has intimate and widespread relations to comparative anatomy, embryology, morphology, zoology, physiology, and anthropology—I shall limit myself to the attempt to bring before you some of the more important observations and conclusions which have a bearing on the present position of the subject. As this is the closing year of the century it will not, I think, be out of place to refer to the changes which a hundred years have brought about in our fundamental conceptions of the structure of animals. In science, as in business, it is well from time to time to take stock of what we have been doing, so that we may realise where we stand and ascertain the balance to our credit in the scientific ledger.

So far back as the time of the ancient Greeks it was known that the human body and those of the more highly organised animals were not homogeneous, but were built up of parts, the *partes dissimilares* (τὰ ἀνόμοια μέρη) of Aristotle, which differed from each other in form, colour, texture, consistency, and properties. These parts were familiarly known as the bones, muscles, sinews, blood-vessels, glands, brain, nerves, and so on. As the centuries rolled on, and as observers and observations multiplied, a more and more precise knowledge of these parts throughout the Animal Kingdom was obtained, and various attempts were made to classify animals in accordance with their forms and structure. During the concluding years of the last century and the earlier part of the present, the Hunters, William and John, in our country, the Meckels in Germany, Cuvier and St. Hilaire in France, gave an enormous impetus to anatomical studies, and contributed largely to our knowledge of the construction of the bodies of animals. But whilst by these and other observers the most salient, and, if I may use the expression, the grosser characters of animal organisation had been recognised, little was known of the more intimate structure or texture of the parts. So far as could be determined by the unassisted vision, and so much as could be recognised by the use of a simple lens, had indeed been ascertained, and it was known that muscles, nerves, and tendons were composed of threads or fibres, that the blood- and lymph-vessels were tubes, that the parts which we call fasciæ and aponeuroses, were thin membranes, and so on.

Early in the present century Xavier Bichat, one of the most brilliant men of science during the Napoleonic era in France, published his "*Anatomie Générale*," in which he formulated important general principles. Every animal is an assemblage of different organs, each of which discharges a function, and acting together, each in

its own way, assists in the preservation of the whole. The organs are, as it were, special machines situated in the general building which constitutes the factory or body of the individual. But, further, each organ or special machine is itself formed of tissues which possess different properties. Some, as the blood-vessels, nerves, fibrous tissues, &c., are generally distributed throughout the animal body, whilst others, as bones, muscles, cartilage, &c., are found only in certain definite localities. Whilst Bichat had acquired a definite philosophical conception of the general principles of construction and of the distribution of the tissues, neither he nor his pupil Béclard was in a position to determine the essential nature of the structural elements. The means and appliances at their disposal and at that of other observers in their generation were not sufficiently potent to complete the analysis.

Attempts were made in the third decennium of this century to improve the methods of examining minute objects by the manufacture of compound lenses, and, by doing away with chromatic and spherical aberration, to obtain, in addition to magnification of the object, a relatively large flat field of vision with clearness and sharpness of definition. When in January, 1830, Joseph Jackson Lister read to the Royal Society his memoir "*On some Properties in Achromatic Object-Glasses applicable to the Improvement of Microscopes*," he announced the principles on which combinations of lenses could be arranged, which would possess these qualities. By the skill of our opticians, microscopes have now for more than half a century been constructed which, in the hands of competent observers, have influenced and extended biological science with results comparable to those obtained by the astronomer through improvements in the telescope.

In the study of the minute structure of plants and animals the observer has frequently to deal with tissues and organs, most of which possess such softness and delicacy of substance and outline that, even when microscopes of the best construction are employed, the determination of the intimate nature of the tissue, and the precise relation which one element of an organ bears to the other constituent elements, is in many instances a matter of difficulty. Hence additional methods have had to be devised in order to facilitate study and to give precision and accuracy to our observations. It is difficult for one of the younger generation of biologists, with all the appliances of a well-equipped laboratory at his command, with experienced teachers to direct him in his work, and with excellent text-books, in which the modern methods are described, to realise the conditions under which his predecessors worked half a century ago. Laboratories for minute biological research had not been constructed, the practical teaching of histology and embryology had not been organised, experience in methods of work had not accumulated; each man was left to his individual efforts, and had to puzzle his way through the complications of structure to the best of his power. Staining and hardening reagents were unknown. The double-bladed knife invented by Valentin, held in the hand, was the only improvement on the scalpel or razor for cutting thin, more or less translucent slices suitable for microscopic examination; mechanical section-cutters and freezing arrangements had not been devised. The tools at the disposal of the microscopist were little more than knife, forceps, scissors, needles; with acetic acid, glycerine, and Canada balsam as reagents. But in the employment of the newer methods of research care has to be taken, more especially when hardening and staining reagents are used, to discriminate between appearances which are to be interpreted as indicating natural characters, and those which are only artificial productions.

Notwithstanding the difficulties attendant on the study of the more delicate tissues, the compound achromatic microscope provided anatomists with an instrument of great penetrative power. Between the years 1830 and 1850 a number of acute observers applied themselves

with much energy and enthusiasm to the examination of the minute structure of the tissues and organs in plants and animals.

Cell Theory.

It had, indeed, long been recognised that the tissues of plants were to a large extent composed of minute vesicular bodies, technically called cells (Hooke, Malpighi, Grew). In 1831 the discovery was made by the great botanist, Robert Brown, that in many families of plants a circular spot, which he named areola or nucleus, was present in each cell; and in 1838 M. J. Schleiden published the fact that a similar spot or nucleus was a universal elementary organ in vegetables. In the tissues of animals also structures had begun to be recognised comparable with the cells and nuclei of the vegetable tissues; and in 1839 Theodore Schwann announced the important generalisation that there is one universal principle of development for the elementary part of organisms, however different they may be in appearance, and that this principle is the formation of cells. The enunciation of the fundamental principle that the elementary tissues consisted of cells constituted a step in the progress of biological science, which will for ever stamp the century now drawing to a close with a character and renown equalling those which it has derived from the most brilliant discoveries in the physical sciences. It provided biologists with the visible anatomical units through which the external forces operating on, and the energy generated in, living matter come into play. It dispelled for ever the old mystical idea of the influence exercised by vapours or spirits in living organisms. It supplied the physiologist and pathologist with the specific structures through the agency of which the functions of organisms are discharged in health and disease. It exerted an enormous influence on the progress of practical medicine. A review of the progress of knowledge of the cell may appropriately enter into an address on this occasion.

Structure of Cells.

A cell is a living particle, so minute that it needs a microscope for its examination; it grows in size, maintains itself in a state of activity, responds to the action of stimuli, reproduces its kind, and in the course of time it degenerates and dies.

Let us glance at the structure of a cell to determine its constituent parts and the rôle which each plays in the function to be discharged. The original conception of a cell, based upon the study of the vegetable tissues, was a minute vesicle enclosed by a definite wall, which exercised chemical or metabolic changes on the surrounding material and secreted into the vesicle its characteristic contents. A similar conception was at first also entertained regarding the cells of animal tissues; but as observations multiplied, it was seen that numerous elementary particles, which were obviously in their nature cells, did not possess an enclosing envelope. A wall ceased to have a primary value as a constituent part of a cell, the necessary vesicular character of which therefore could no longer be entertained.

The other constituent parts of a cell are the cell plasma, which forms the body of the cell, and the nucleus embedded in its substance. Notwithstanding the very minute size of the nucleus, which even in the largest cells is not more than 1/500th inch in diameter, and usually is considerably smaller, its almost constant form, its well-defined sharp outline, and its power of resisting the action of strong reagents when applied to the cell, have, from the period of its discovery by Robert Brown, caused histologists to bestow on it much attention. Its structure and chemical composition, its mode of origin, the part which it plays in the formation of new cells, and its function in nutrition and secretion, have been investigated.

When examined under favourable conditions in its passive or resting state, the nucleus is seen to be bounded by a membrane which separates it from the cell-plasma and gives it the characteristic sharp contour. It contains

an apparently structureless nuclear substance, nucleoplasm or enchylema, in which are embedded one or more extremely minute particles called nucleoli, along with a network of exceedingly fine threads or fibres, which in the active living cell play an essential part in the production of new nuclei within the cell. In its chemical composition the nuclear substance consists of albuminous plastin and globulin; and of a special material named nuclein, rich in phosphorus and with an acid reaction. The delicate network within the nucleus consists apparently of the nuclein, a substance which stains with carmine and other dyes, a property which enables the changes, which take place in the network in the production of young cells, to be more readily seen and followed out by the observer.

The mode of origin of the nucleus and the part which it plays in the production of new cells have been the subject of much discussion. Schleiden, whose observations, published in 1838, were made on the cells of plants, believed that within the cell a nucleolus first appeared, and that around it molecules aggregated to form the nucleus. Schwann again, whose observations were mostly made on the cells of animals, considered that an amorphous material existed in organised bodies, which he called cytoblastema. It formed the contents of cells, or it might be situated free or external to them. He figuratively compared it to a mother-liquor in which crystals are formed. Either in the cytoblastema within the cells or in that situated external to them, the aggregation of molecules around a nucleolus to form a nucleus might occur, and, when once the nucleus had been formed, in its turn it would serve as a centre of aggregation of additional molecules from which a new cell would be produced. He regarded therefore the formation of nuclei and cells as possible in two ways; one within pre-existing cells (endogenous cell-formation), the other in a free blastema lying external to cells (free cell-formation). In animals, he says, the endogenous method is rare, and the customary origin is in an external blastema. Both Schleiden and Schwann considered that after the cell was formed the nucleus had no permanent influence on the life of the cell, and usually disappeared.

Under the teaching principally of Henle, the famous Professor of Anatomy in Göttingen, the conception of the free formation of nuclei and cells in a more or less fluid blastema, by an aggregation of elementary granules and molecules, obtained so much credence, especially amongst those who were engaged in the study of pathological processes, that the origin of cells within pre-existing cells was to a large extent lost sight of. That a parent cell was requisite for the production of new cells seemed to many investigators to be no longer needed. Without doubt this conception of free cell-formation contributed in no small degree to the belief, entertained by various observers, that the simplest plants and animals might arise, without pre-existing parents, in organic fluids destitute of life, by a process of spontaneous generation—a belief which prevailed in many minds almost to the present day. If, as has been stated, the doctrine of abiogenesis cannot be experimentally refuted, on the other hand it has not been experimentally proved. The burden of proof lies with those who hold the doctrine, and the evidence that we possess is all the other way.

Multiplication of Cells.

Although von Mohl, the botanist, seems to have been the first to recognise (1835) in plants a multiplication of cells by division, it was not until attention was given to the study of the egg in various animals, and to the changes which take place in it, attendant on fertilisation, that in the course of time a much more correct conception of the origin of the nucleus and of the part which it plays in the formation of new cells was obtained. Before Schwann had published his classical memoir in 1839, von Baer and other observers had recognised within the animal ovum the germinal vesicle, which obviously bore to the ovum

the relation of a nucleus to a cell. As the methods of observation improved, it was recognised that, within the developing egg, two vesicles appeared where one only had previously existed, to be followed by four vesicles, then eight, and so on in multiple progression until the ovum contained a multitude of vesicles, each of which possessed a nucleus. The vesicles were obviously cells which had arisen within the original germ-cell or ovum. These changes were systematically described by Martin Barry so long ago as 1839 and 1840 in two memoirs communicated to the Royal Society of London, and the appearance produced, on account of the irregularities of the surface occasioned by the production of new vesicles, was named by him the mulberry-like structure. He further pointed out that the vesicles arranged themselves as a layer within the envelope of the egg or zona pellucida, and that the whole embryo was composed of cells filled with the foundations of other cells. He recognised that the new cells were derived from the germinal vesicle or nucleus of the ovum, the contents of which entered into the formation of the first two cells, each of which had its nucleus, which in its turn resolved itself into other cells, and by a repetition of the process into a greater number. The endogenous origin of new cells within a pre-existing cell, and the process which we now term the segmentation of the yolk, were successfully demonstrated. In a third memoir, published in 1841, Barry definitely stated that young cells originated through division of the nucleus of the parent cell, instead of arising, as a product of crystallisation, in the fluid cytoplasm of the parent cell, or in a blastema situated external to the cell.

In a memoir published in 1842, John Goodsir advocated the view that the nucleus is the reproductive organ of the cell, and that from it, as from a germinal spot, new cells were formed. In a paper, published three years later, on nutritive centres, he described cells, the nuclei of which were the permanent source of successive broods of young cells, which from time to time occupied the cavity of the parent cell. He extended also his observations on the endogenous formation of cells to the cartilage cells in the process of inflammation, and to other tissues undergoing pathological changes. Corroborative observations on endogenous formation were also given by his brother, Harry Goodsir, in 1845. These observations on the part which the nucleus plays by cleavage in the formation of young cells by endogenous development from a parent centre—that an organic continuity existed between a mother cell and its descendants through the nucleus—constituted a great step in advance of the views entertained by Schleiden and Schwann, and showed that Barry and the Goodsirs had a deeper insight into the nature and functions of cells than was possessed by most of their contemporaries, and are of the highest importance when viewed in the light of recent observations.

In 1841 Robert Remak published an account of the presence of two nuclei in the blood corpuscles of the chick and the pig, which he regarded as evidence of the production of new corpuscles by division of the nucleus within a parent cell; but it was not until some years afterwards (1850 to 1855) that he recorded additional observations, and recognised that division of the nucleus was the starting-point for the multiplication of cells in the ovum and in the tissues generally. Remak's view was that the process of cell division began with the cleavage of the nucleolus, followed by that of the nucleus, and that again by cleavage of the body of the cell and of its membrane. Kölliker had previously, in 1843, described the multiplication of nuclei in the ova of parasitic worms, and drew the inference that in the formation of young cells within the egg the nucleus underwent cleavage, and that each of its divisions entered into the formation of a new cell. By these observations, and by others subsequently made, it became obvious that the multiplication of animal cells, either by division of the nucleus within the cell, or by the budding off of a part of the protoplasm of the cell, was to be regarded as a widely spread and probably a

universal process, and that each new cell arose from a parent cell.

Pathological observers were, however, for the most part inclined to consider free cell-formation in a blastema or exudation by an aggregation of molecules, in accordance with the views of Hienle, as a common phenomenon. This proposition was attacked with great energy by Virchow in a series of memoirs published in his "Archiv," commencing in Vol. I., 1847, and finally received its death-blow in his published lectures on Cellular Pathology, 1858. He maintained that in pathological structures there was no instance of cell development *de novo*; where a cell existed, there one must have been before. Cell-formation was a continuous development by descent, which he formulated in the expression *omnis cellula e cellula*.

Karyokinesis.

Whilst the descent of cells from pre-existing cells by division of the nucleus during the development of the egg, in the embryos of plants and animals, and in adult vegetable and animal tissues, both in healthy and diseased conditions, had now become generally recognised, the mechanism of the process by which the cleavage of the nucleus took place was for a long time unknown. The discovery had to be deferred until the optician had been able to construct lenses of a higher penetrative power, and the microscopist had learned the use of colouring agents capable of dyeing the finest elements of the tissues. There was reason to believe that in some cases a direct cleavage of the nucleus, to be followed by a corresponding division of the cell into two parts, did occur. In the period between 1870 and 1880 observations were made by Schneider, Strasburger, Bütschli, Fol, van Beneden, and Flemming, which showed that the division of the nucleus and the cell was due to a series of very remarkable changes, now known as indirect nuclear and cell division, or karyokinesis. The changes within the nucleus are of so complex a character that it is impossible to follow them in detail without the use of appropriate illustrations. I shall have to content myself, therefore, with an elementary sketch of the process.

I have previously stated that the nucleus in its passive or resting stage contains a very delicate network of threads or fibres. The first stage in the process of nuclear division consists in the threads arranging themselves in loops, and forming a compact coil within the nucleus. The coil then becomes looser, the loops of threads shorten and thicken, and somewhat later each looped thread splits longitudinally into two portions. As the threads stain when colouring agents are applied to them, they are called chromatin fibres, and the loose coil is the chromosome (Waldayer).

As the process continues, the investing membrane of the nucleus disappears, and the loops of threads arrange themselves within the nucleus, so that the closed ends of the loops are directed to a common centre, from which the loops radiate outwards, and produce a star-like figure (aster). At the same time clusters of extremely delicate lines appear both in the nucleoplasm and in the body of the cell, named the achromatic figure, which has a spindle-like form with two opposite poles, and stains much more feebly than the chromatin fibres. The loops of the chromatin star then arrange themselves in the equatorial plane of the spindle, and bending round turn their closed ends towards the periphery of the nucleus and the cell.

The next stage marks an important step in the process of division of the nucleus. The two longitudinal portions, into which each looped thread had previously split, now separate from each other, and whilst one part migrates to one pole of the spindle, the other moves to the opposite pole, and the free ends of each loop are directed towards its equator (metakinesis). By this division of the chromatin fibres, and their separation from each other to opposite poles of the spindle, two star-like chromatin figures are produced (dyaster).

Each group of fibres thickens, shortens, becomes surrounded by a membrane, and forms a new or daughter nucleus (dispirem). Two nuclei therefore have arisen within the cell by the division of that which had previously existed, and the expression formulated by Flemming—*omnis nucleus e nucleo*—is justified. Whilst this stage is in course of being completed, the body of the cell becomes constricted in the equatorial plane of the spindle, and, as the constriction deepens, it separates into two parts, each containing a daughter nucleus, so that two nucleated cells have arisen out of a pre-existing cell.

A repetition of the process in each of these cells leads to the formation of other cells, and, although modifications in details are found in different species of plants and animals, the multiplication of cells in the egg and in the tissues generally on similar lines is now a thoroughly established fact in biological science.

In the study of karyokinesis, importance has been attached to the number of chromosomes in the nucleus of the cell. Flemming had seen in the Salamander twenty-four chromosome fibres, which seems to be a constant number in the cells of epithelium and connective tissues. In other cells, again, especially in the ova of certain animals, the number is smaller, and fourteen, twelve, four, and even two only have been described. The theory formulated by Boveri that the number of chromosomes is constant for each species, and that in the karyokinetic figures corresponding numbers are found in homologous cells, seems to be not improbable.

In the preceding description I have incidentally referred to the appearance in the proliferating cell of an achromatic spindle-like figure. Although this was recognised by Fol in 1873, it is only during the last ten or twelve years that attention has been paid to its more minute arrangements and possible signification in cell division.

The pole at each end of the spindle lies in the cell plasm which surrounds the nucleus. In the centre of each pole is a somewhat opaque spot (central body) surrounded by a clear space, which, along with the spot, constitutes the centrosome or the sphere of attraction. From each centrosome extremely delicate lines may be seen to radiate in two directions. One set extends towards the pole at the opposite end of the spindle, and, meeting or coming into close proximity with radiations from it, constitutes the body of the spindle, which, like a perforated mantle, forms an imperfect envelope around the nucleus during the process of division. The other set of radiations is called the polar, and extends in the region of the pole towards the periphery of the cell.

The question has been much discussed whether any constituent part of the achromatic figure, or the entire figure, exists in the cell as a permanent structure in its resting phase; or if it is only present during the process of karyokinesis. During the development of the egg the formation of young cells, by division of the segmentation nucleus, is so rapid and continuous that the achromatic figure, with the centrosome in the pole of the spindle, is a readily recognisable object in each cell. The polar and spindle-like radiations are in evidence during karyokinesis, and have apparently a temporary endurance and function. On the other hand, van Beneden and Boveri were of opinion that the central body of the centrosome did not disappear when the division of the nucleus came to an end, but that it remained as a constituent part of a cell lying in the cell plasm near to the nucleus. Flemming has seen the central body with its sphere in leucocytes, as well as in epithelial cells and those of other tissues. Subsequently Heidenhain and other histologists have recorded similar observations. It would seem, therefore, as if there were reason to regard the centrosome, like the nucleus, as a permanent constituent of a cell. This view, however, is not universally entertained. If not always capable of demonstration in the resting stage of a cell, it is doubtless to be regarded as potentially present, and ready to assume, along with the radiations, a characteristic

appearance when the process of nuclear division is about to begin.

One can scarcely regard the presence of so remarkable an appearance as the achromatic figure without associating with it an important function in the economy of the cell. As from the centrosome at the pole of the spindle both sets of radiations diverge, it is not unlikely that it acts as a centre or sphere of energy and attraction. By some observers the radiations are regarded as substantive fibrillar structures, elastic or even contractile in their properties. Others, again, look upon them as morphological expressions of chemical and dynamical energy in the protoplasm of the cell body. On either theory we may assume that they indicate an influence, emanating, it may be, from the centrosome, and capable of being exercised both on the cell plasm and on the nucleus contained in it. On the contractile theory, the radiations which form the body of the spindle: either by actual traction of the supposed fibrillæ or by their pressure on the nucleus which they surround, might impel during karyokinesis the dividing chromosome elements towards the poles of the spindle, to form there the daughter nuclei. On the dynamical theory, the chemical and physical energy in the centrosome might influence the cell plasm and the nucleus, and attract the chromosome elements of the nucleus to the poles of the spindle. The radiated appearance would therefore be consequent and attendant on the physico-chemical activity of the centrosome. One or other of these theories may also be applied to the interpretation of the significance of the polar radiations.

Cell Plasm.

In the cells of plants, in addition to the cell wall, the cell body and the cell juice require to be examined. The material of the cell body, or the cell contents, was named by von Mohl (1846) protoplasm, and consisted of a colourless tenacious substance, which partly lined the cell wall (primordial utricle), and partly traversed the interior of the cell as delicate threads enclosing spaces (vacuoles) in which the cell juice was contained. In the protoplasm the nucleus was embedded. Nägeli, about the same time, had also recognised the difference between the protoplasm and the other contents of vegetable cells, and had noticed its nitrogenous composition.

Though the analogy with a closed bladder or vesicle could no longer be sustained in the animal tissues, the name "cell" continued to be retained for descriptive purposes, and the body of the cell was spoken of as a more or less soft substance enclosing a nucleus (Leydig). In 1861 Max Schultze adopted for the substance forming the body of the animal cell the term "protoplasm." He defined a cell to be a particle of protoplasm in the substance of which a nucleus was situated. He regarded the protoplasm, as indeed had previously been pointed out by the botanist, Unger, as essentially the same as the contractile sarcode which constitutes the body and pseudopodia of the *Amoeba* and other *Rhizopoda*. As the term "protoplasm," as well as that of "bioplasm" employed by Lionel Beale in a somewhat similar though not precisely identical sense, involves certain theoretical views of the origin and function of the body of the cell, it would be better to apply to it the more purely descriptive term, "cytoplasm" or "cell plasm."

Schultze defined protoplasm as a homogeneous, glassy, tenacious material, of a jelly-like or somewhat firmer consistency, in which numerous minute granules were embedded. He regarded it as the part of the cell especially endowed with vital energy, whilst the exact function of the nucleus could not be defined. Based upon this conception of the jelly-like character of protoplasm, the idea for a time prevailed that a structureless, dimly granular, jelly or slime destitute of organisation, possessed great physiological activity, and was the medium through which the phenomena of life were displayed.

More accurate conceptions of the nature of the cell plasm soon began to be entertained. Büccke recognised

that the body of the cell was not simple, but had a complex organisation. Flemming observed that the cell plasma contained extremely delicate threads, which frequently formed a network, the interspaces of which were occupied by a more homogeneous substance. Where the threads crossed each other, granular particles (mikrosomen) were situated. Bütschli considered that he could recognise in the cell plasma a honeycomb-like appearance, as if it consisted of excessively minute chambers in which a homogeneous more or less fluid material was contained. The polar and spindle-like radiations visible during the process of karyokinesis, which have already been referred to, and the presence of the centrosome, possibly even during the resting stage of the cell, furnished additional illustrations of differentiation within the cell plasma. In many cells there appears also to be a difference in the character of the cell plasma which immediately surrounds the nucleus, and that which lies at and near the periphery of the cell. The peripheral part (ektoplasma) is more compact, and gives a definite outline to the cell, although not necessarily differentiating into a cell membrane. The inner part (endoplasma) is softer, and is distinguished by a more distinct granular appearance, and by containing the products specially formed in each particular kind of cell during the nutritive process.

By the researches of numerous investigators on the internal organisation of cells in plants and animals, a large body of evidence has now been accumulated, which shows that both the nucleus and the cell plasma consist of something more than a homogeneous, more or less viscid, slimy material. Recognisable objects in the form of granules, threads, or fibres can be distinguished in each. The cell plasma and the nucleus respectively are therefore not of the same constitution throughout, but possess polymorphic characters, the study of which in health and the changes produced by disease will for many years to come form important matters for investigation.

Function of Cells.

It has already been stated that, when new cells arise within pre-existing cells, division of the nucleus is associated with cleavage of the cell plasma, so that it participates in the process of new cell-formation. Undoubtedly, however, its rôle is not limited to this function. It also plays an important part in secretion, nutrition, and the special functions discharged by the cells in the tissues and organs of which they form morphological elements.

Between 1838 and 1842 observations were made which showed that cells were constituent parts of secreting glands and mucous membranes (Schwann, Henle). In 1842 John Goodsir communicated to the Royal Society of Edinburgh a memoir on secreting structures, in which he established the principle that cells are the ultimate secreting agents; he recognised in the cells of the liver, kidney, and other organs the characteristic secretion of each gland. The secretion was, he said, situated between the nucleus and the cell wall. At first he thought that, as the nucleus was the reproductive organ of the cell, the secretion was formed in the interior of the cell by the agency of the cell wall; but three years later he regarded it as a product of the nucleus. The study of the process of spermatogenesis by his brother, Harry Goodsir, in which the head of the spermatozoon was found to correspond with the nucleus of the cell in which the spermatozoon arose, gave support to the view that the nucleus played an important part in the genesis of the characteristic product of the gland cell.

The physiological activity of the cell plasma and its complex chemical constitution soon after began to be recognised. Some years before Max Schultze had published his memoirs on the characters of protoplasm, Brücke had shown that the well known changes in tint in the skin of the *Chamæleon* were due to pigment granules situated in cells in the skin, which were sometimes diffused throughout the cells, at others concentrated in the centre. Similar observations on the skin of the frog

were made in 1854 by von Wittich and Harless. The movements were regarded as due to contraction of the cell wall on its contents. In a most interesting paper on the pigmentary system in the frog, published in 1858, Lord Lister demonstrated that the pigment granules moved in the cell plasma, by forces resident within the cell itself, acting under the influence of an external stimulant, and not by a contractility of the wall. Under some conditions the pigment was attracted to the centre of the cell, when the skin became pale; under other conditions the pigment was diffused throughout the body and the branches of the cell, and gave to the skin a dark colour. It was also experimentally shown that a potent influence over these movements was exercised by the nervous system.

The study of the cells of glands engaged in secretion, even when the secretion is colourless, and the comparison of their appearance when secretion is going on with that seen when the cells are at rest, have shown that the cell plasma is much more granular and opaque, and contains larger particles during activity than when the cell is passive; the body of the cell swells out from an increase in the contents of its plasma, and chemical changes accompany the act of secretion. Ample evidence, therefore, is at hand to support the position taken by John Goodsir, nearly sixty years ago, that secretions are formed within cells, and lie in that part of the cell which we now say consists of the cell plasma; that each secreting cell is endowed with its own peculiar property, according to the organ in which it is situated, so that bile is formed by the cells in the liver, milk by those in the mamma, and so on.

Intimately associated with the process of secretion is that of nutrition. As the cell plasma lies at the periphery of a cell, and as it is, alike both in secretion and nutrition, brought into closest relation with the surrounding medium, from which the pabulum is derived, it is necessarily associated with nutritive activity. Its position enables it to absorb nutritive material directly from without, and in the process of growth it increases in amount by interstitial changes and additions throughout its substance, and not by mere accretions on its surface.

Hitherto I have spoken of a cell as a unit, independent of its neighbours as regards its nutrition, and the other functions which it has to discharge. The question has, however, been discussed, whether in a tissue composed of cells closely packed together, cell plasma may not give origin to processes or threads which are in contact or continuous with corresponding processes of adjoining cells, and that cells may therefore, to some extent, lose their individuality in the colony of which they are members. Appearances were recognised between 1863 and 1870 by Schrön and others in the deeper cells of the epidermis, and of some mucous membranes which gave sanction to this view, and it seems possible, through contact or continuity of threads connecting a cell with its neighbours, that cells may exercise a direct influence on each other.

Nägeli, the botanist, as the foundation of a mechanico-physiological theory of descent, considered that in plants a network of cell plasma, named by him *idio-plasm*, extended throughout the whole of the plant, forming its specific molecular constitution, and that growth and activity were regulated by its conditions of tension and movements (1884).

The study of the structure of plants, with special reference to the presence of an intercellular network, has for some years been pursued by Walter Gardiner (1882-97), who has demonstrated threads of cell plasma protruding through the walls of vegetable cells, and continuous with similar threads from adjoining cells. Structurally, therefore, a plant may be conceived to be built up of a nucleated cytoplasmic network, each nucleus with the branching cell plasma surrounding it being a centre of activity. On this view a cell would retain, to some extent, its individuality, though, as Gardiner contends, the connecting

threads would be the medium for the conduction of impulses and of food from a cell to those which lie around it. For the plant cell, therefore, as has long been accepted in the animal cell, the wall is reduced to a secondary position, and the active constituent is the nucleated cell plasm. It is not unlikely that the absence of a controlling nervous system in plants requires the plasm of adjoining cells to be brought into more immediate contact and continuity than is the case with the generality of animal cells, so as to provide a mechanism for harmonising the nutritive and other functional processes in the different areas in the body of the plant. In this particular it is of interest to note that the epithelial tissues in animals, where somewhat similar connecting arrangements occur, are only indirectly associated with the nervous and vascular systems, so that, as in plants, the cells may require, for nutritive and other purposes, to act and re-act directly on each other.

Nerve Cells.

Of recent years great attention has been paid to the intimate structure of nerve cells, and to the appearance which they present when in the exercise of their functional activity. A nerve cell is not a secreting cell; that is, it does not derive from the blood or surrounding fluid a pabulum, which it elaborates into a visible, palpable secretion, characteristic of the organ of which the cell is a constituent element, to be in due course discharged into a duct which conveys the secretion out of the gland. Nerve cells, through the metabolic changes which take place in them in connection with their nutrition, are associated with the production of the form of energy specially exhibited by animals which possess a nervous system, termed nerve energy. It has long been known that every nerve cell has a body in which a relatively large nucleus is situated. A most important discovery was the recognition that the body of every nerve cell had one or more processes growing out from it. More recently it has been proved, chiefly through the researches of Schultze, His, Golgi, and Ramon y Cajal, that at least one of the processes, the axon of the nerve cell, is continued into the axial cylinder of a nerve fibre, and that in the multipolar nerve cell the other processes, or dendrites, branch and ramify for some distance away from the body. A nerve fibre is therefore an essential part of the cell with which it is continuous, and the cell, its processes, the nerve fibre, and the collaterals which arise from the nerve fibre collectively form a neuron or structural nerve unit (Waldeyer). The nucleated body of the nerve cell is the physiological centre of the unit.

The cell plasm occupies both the body of the nerve cell and its processes. The intimate structure of the plasm has, by improved methods of observation introduced during the last eight years by Nissl, and conducted on similar lines by other investigators, become more definitely understood. It has been ascertained that it possesses two distinct characters which imply different structures. One of these stains deeply on the addition of certain dyes, and is named chromophile or chromatic substance; the other, which does not possess a similar property, is the achromatic network. The chromophile is found in the cell body and the dendritic processes, but not in the axon. It occurs in the form of granular particles, which may be scattered throughout the plasm, or aggregated into little heaps which are elongated or fusiform in shape, and appear as distinct coloured particles or masses. The achromatic network is found in the cell body and the dendrites, and is continued also into the axon, where it forms the axial cylinder of the nerve fibre. It consists apparently of delicate threads or fibrillæ, in the meshes of which a homogeneous material, such as is found in cell plasm generally, is contained. In the nerve cells, as in other cells, the plasm is, without doubt, concerned in the process of cell nutrition. The achromatic fibrillæ exercise an important influence on the axon or nerve fibre with which they are continuous, and probably they conduct the nerve impulses which manifest themselves in the form of

nerve energy. The dendritic processes of a multipolar nerve cell ramify in close relation with similar processes branching from other cells in the same group. The collaterals and the free end of the axon fibre process branch and ramify in association with the body of a nerve cell or of its dendrites. We cannot say that these parts are directly continuous with each other to form an inter-cellular network, but they are apparently in apposition, and through contact exercise influence one on the other in the transmission of nerve impulses.

There is evidence to show that in the nerve cell the nucleus, as well as the cell plasm, is an effective agent in nutrition. When the cell is functionally active, both the cell body and the nucleus increase in size (Vas, G. Mann, Lugaro); on the other hand, when nerve cells are fatigued through excessive use, the nucleus decreases in size and shrivels; the cell plasm also shrinks, and its coloured or chromophile constituent becomes diminished in quantity, as if it had been consumed during the prolonged use of the cell (Hodge, Mann, Lugaro). It is interesting also to note that in hibernating animals in the winter season, when their functional activity is reduced to a minimum, the chromophile in the plasm of the nerve cells is much smaller in amount than when the animal is leading an active life in the spring and summer (G. Levi).

When a nerve cell has attained its normal size, it does not seem to be capable of reproducing new cells in its substance by a process of karyokinesis, such as takes place when young cells arise in the egg and in the tissues generally. It would appear that nerve cells are so highly specialised in their association with the evolution of nerve energy, that they have ceased to have the power of reproducing their kind, and the metabolic changes, both in cell plasm and nucleus, are needed to enable them to discharge their very peculiar function. Hence it follows that when a portion of the brain or other nerve-centre is destroyed, the injury is not repaired by the production of fresh specimens of their characteristic cells, as would be the case in injuries to bones and tendons.

In our endeavours to differentiate the function of the nucleus from that of the cell plasm, we should not regard the former as concerned only in the production of young cells, and the latter as the exclusive agent in growth, nutrition, and, where gland cells are concerned, in the formation of their characteristic products. As regards cell reproduction also, though the process of division begins in the nucleus in its chromosome constituents, the achromatic figure in the cell plasm undoubtedly plays a part, and the cell plasm itself ultimately undergoes cleavage.

A few years ago the tendency amongst biologists was to ignore or attach but little importance to the physiological use of the nucleus in the nucleated cell, and to regard the protoplasm as the essential and active constituent of living matter; so much so, indeed, was this the case that independent organisms regarded as distinct species were described as consisting of protoplasm destitute of a nucleus; also that scraps of protoplasm separated from larger nucleated masses could, when isolated, exhibit vital phenomena. There is reason to believe that a fragment of protoplasm, when isolated from the nucleus of a cell, though retaining its contractility and capable of nourishing itself for a short time, cannot increase in amount, act as a secreting structure, or reproduce its kind; it soon loses its activity, withers, and dies. In order that these qualities of living matter should be retained, a nucleus is, by most observers, regarded as necessary (Nussbaum, Gruber, Haberlandt, Korschelt), and for the complete manifestation of vital activity both nucleus and cell plasm are required.

Bacteria.

The observations of Cohn, made about thirty years ago, and those of De Bary shortly afterwards, brought into notice a group of organisms, to which the name "bacterium" or "microbe" is given. They were seen to vary in shape; some were rounded specks called cocci, others were straight rods called bacilli, others were curved

or spiral rods, vibrios or spirillæ. All were characterised by their extreme minuteness, and required for their examination the highest powers of the best microscopes. Many bacteria measure in their least diameter not more than $1/25,000$ th of an inch, one-tenth the diameter of a human white blood corpuscle. Through the researches of Pasteur, Lord Lister, Koch, and other observers, bacteria have been shown to play an important part in nature. They exercise a very remarkable power over organic substances, especially those which are complex in chemical constitution, and can resolve them into simpler combinations. Owing to this property, some bacteria are of great economic value, and without their agency many of our industries could not be pursued; others, again, and these are the most talked of, exercise a malign influence in the production of the most deadly diseases which afflict man and the domestic animals.

Great attention has been given to the structure of bacteria and to their mode of propagation. When examined in the living state and magnified about 2000 times, a bacterium appears as a homogeneous particle, with a sharp definite outline, though a membranous envelope or wall, distinct from the body of the bacterium, cannot at first be recognised; but when treated with reagents a membranous envelope appears, the presence of which, without doubt, gives precision of form to the bacterium. The substance within the membrane contains granules which can be dyed with colouring agents. Owing to their extreme minuteness, it is difficult to pronounce an opinion on the nature of the chromatic granules and the substance in which they lie. Some observers regard them as nuclear material, invested by only a thin layer of protoplasm, on which view a bacterium would be a nucleated cell. Others consider the bacterium as formed of protoplasm containing granules capable of being coloured, which are a part of the protoplasm itself, and not a nuclear substance. On the latter view, bacteria would consist of cell plasma enclosed in a membrane and destitute of a nucleus. Whatever be the nature of the granule-containing material, each bacterium is regarded as a cell, the minutest and simplest living particle capable of an independent existence that has yet been discovered.

Bacteria cells, like cells generally, can reproduce their kind. They multiply by simple fission, probably with an ingrowth of the cell wall, but without the karyokinetic phenomena observed in nucleated cells. Each cell gives rise to two daughter cells, which may for a time remain attached to each other and form a cluster or a chain, or they may separate and become independent isolated cells. The multiplication, under favourable conditions of light, air, temperature, moisture and food, goes on with extraordinary rapidity, so that in a few hours many thousand new individuals may arise from a parent bacterium.

Connected with the life-history of a bacterium cell is the formation in its substance, in many species and under certain conditions, of a highly refractile shiny particle called a spore. At first sight a spore seems as if it were the nucleus of the bacterium cell, but it is not always present when multiplication by cleavage is taking place, and when present it does not appear to take part in the fission. On the other hand, a spore, from the character of its envelope, possesses great power of resistance, so that dried bacteria, when placed in conditions favourable to germination, can through their spores germinate and resume an active existence. Spore formation seems, therefore, to be a provision for continuing the life of the bacterium under conditions which, if spores had not formed, would have been the cause of its death.

The time has gone by to search for the origin of living organisms by a spontaneous aggregation of molecules in vegetable or other infusions, or from a layer of formless primordial slime diffused over the bed of the ocean. Living matter during our epoch has been, and continues to be, derived from pre-existing living matter, even when it possesses the simplicity of structure of a bacterium, and the morphological unit is the cell.

Development of the Egg.

As the future of the entire organism lies in the fertilised egg cell, we may now briefly review the arrangements, consequent on the process of segmentation, which lead to the formation let us say in the egg of a bird, of the embryo or young chick.

In the latter part of the last century, C. F. Wolff observed that the beginning of the embryo was associated with the formation of layers, and in 1817 Pander demonstrated that in the hen's egg at first one layer, called mucous, appeared, then a second or serous layer, to be followed by a third, intermediate or vascular layer. In 1828 von Baer amplified our knowledge in his famous treatise, which from its grasp of the subject created a new epoch in the science of embryology. It was not, however, until the discovery by Schwann of cells as constant factors in the structure of animals and in their relation to development that the true nature of these layers was determined. We now know that each layer consists of cells, and that all the tissues and organs of the body are derived from them. Numerous observers have devoted themselves for many years to the study of each layer, with the view of determining the part which it takes in the formation of the constituent parts of the body, more especially in the higher animals, and the important conclusion has been arrived at that each kind of tissue invariably arises from one of these layers and from no other.

The layer of cells which contributes, both as regards the number and variety of the tissues derived from it, most largely to the formation of the body is the middle layer or mesoblast. From it the skeleton, the muscles, and other locomotor organs, the true skin, the vascular system, including the blood, and other structures which I need not detail, take their rise. From the inner layer of cells or hypoblast, the principal derivatives are the epithelial lining of the alimentary canal, and of the glands which open into it, and the epithelial lining of the air passages. The outer or epiblast layer of cells gives origin to the epidermis or scarf skin and to the nervous system. It is interesting to note that from the same layer of the embryo arise parts so different in importance as the cuticle—a mere protecting structure, which is constantly being shed when the skin is subjected to the friction of a towel or the clothes—and the nervous system, including the brain, the most highly differentiated system in the animal body. How completely the cells from which they are derived had diverged from each other in the course of their differentiation in structure and properties is shown by the fact that the cells of the epidermis are continually engaged in reproducing new cells to replace those which are shed, whilst the cells of the nervous system have apparently lost the power of reproducing their kind.

In the early stage of the development of the egg, the cells in a given layer resemble each other in form, and, as far as can be judged from their appearance, are alike in structure and properties. As the development proceeds, the cells begin to show differences in character, and in the course of time the tissues which arise in each layer differentiate from each other and can be readily recognised by the observer. To use the language of von Baer, a generalised structure has become specialised, and each of the special tissues produced exhibits its own structure and properties. These changes are coincident with a rapid multiplication of the cells by cleavage, and thus increase in size of the embryo accompanies specialisation of structure. As the process continues, the embryo gradually assumes the shape characteristic of the species to which its parents belonged, until at length it is fit to be born and to assume a separate existence.

The conversion of cells, at first uniform in character, into tissues of a diverse kind is due to forces inherent in the cells in each layer. The cell plasma plays an active though not an exclusive part in the specialisation; for as the nucleus influences nutrition and secretion, it acts as a factor in the differentiation of the tissues. When tissues so diverse in character as muscular fibre, cartilage, fibrous

tissues, and bone arise from the cells of the middle or mesoblast layer, it is obvious that, in addition to the morphological differentiation affecting form and structure, a chemical differentiation affecting composition also occurs, as the result of which a physiological differentiation takes place. The tissues and organs become fitted to transform the energy derived from the food into muscular energy, nerve energy, and other forms of vital activity. Corresponding differentiations also modify the cells of the outer and inner layers. Hence the study of the development of the generalised cell layers in the young embryo enables us to realise how all the complex constituent parts of the body in the higher animals and in man are evolved by the process of differentiation from a simple nucleated cell—the fertilised ovum. A knowledge of the cell and of its life-history is therefore the foundation-stone on which biological science in all its departments is based.

If we are to understand by an organ in the biological sense a complex body capable of carrying on a natural process, a nucleated cell is an organ in its simplest form. In a unicellular animal or plant such an organ exists in its most primitive stage. The higher plants and animals again are built up of multitudes of these organs, each of which, whilst having its independent life, is associated with the others, so that the whole may act in unison for a common purpose. As in one of your great factories each spindle is engaged in twisting and winding its own thread, it is at the same time intimately associated with the hundreds of other spindles in its immediate proximity, in the manufacture of the yarn from which the web of cloth is ultimately to be woven.

It has taken more than fifty years of hard and continuous work to bring our knowledge of the structure and development of the tissues and organs of plants and animals up to the level of the present day. Amidst the host of names of investigators, both at home and abroad, who have contributed to its progress, it may seem invidious to particularise individuals. There are, however, a few that I cannot forbear to mention, whose claim to be named on such an occasion as this will be generally conceded.

Botanists will, I think, acknowledge Wilhelm Hofmeister as a master in morphology and embryology, Julius von Sachs as the most important investigator in vegetable physiology during the last quarter of a century, and Strasburger as a leader in the study of the phenomena of nuclear division.

The researches of the veteran Professor of Anatomy in Würzburg, Albert von Kölliker, have covered the entire field of animal histology. His first paper, published fifty-nine years ago, was followed by a succession of memoirs and books on human and comparative histology and embryology, and culminated in his great treatise on the structure of the brain, published in 1896. Notwithstanding the weight of more than eighty years, he continues to prosecute histological research, and has published the results of his latest, though let us hope not his last, work during the present year.

Amongst our own countrymen, and belonging to the generation which has almost passed away, was William Bowman. His investigations between 1840 and 1850 on the mucous membranes, muscular fibre, and the structure of the kidney, together with his researches on the organs of sense, were characterised by a power of observation and of interpreting difficult and complicated appearances which has made his memoirs on these subjects landmarks in the history of histological inquiry.

Of the younger generation of biologists Francis Maitland Balfour, whose early death is deeply deplored as a loss to British Science, was one of the most distinguished. His powers of observation and philosophic perception gave him a high place as an original enquirer, and the charm of his personality—for charm is not the exclusive possession of the fairer sex—endeared him to his friends.

General Morphology.

Along with the study of the origin and structure of the tissues of organised bodies, much attention has been given during the century to the parts or organs in plants and animals, with the view of determining where and how they take their rise, the order of their formation, the changes which they pass through in the early stages of development, and their relative positions in the organism to which they belong. Investigations on these lines are spoken of as morphological, and are to be distinguished from the study of their physiological or functional relations, though both are necessary for the full comprehension of the living organism.

The first to recognise that morphological relations might exist between the organs of a plant, dissimilar as regards their function, was the poet Goethe, whose observations, guided by his imaginative faculty, led him to declare that the calyx, corolla, and other parts of a flower, the scales of a bulb, &c., were metamorphosed leaves, a principle generally accepted by botanists, and indeed extended to other parts of a plant, which are referred to certain common morphological forms although they exercise different functions. Goethe also applied the same principle in the study of the skeletons of vertebrate animals, and he formed the opinion that the spinal column and the skull were essentially alike in construction, and consisted of vertebrae, an idea which was also independently conceived and advocated by Oken.

The anatomist who in our country most strenuously applied himself to the morphological study of the skeleton was Richard Owen, whose knowledge of animal structure, based upon his own dissections, was unrivalled in range and variety. He elaborated the conception of an ideal, archetype vertebrate form, which had no existence in nature, and to which, subject to modifications in various directions, he considered all vertebrate skeletons might be referred. Owen's observations were conducted to a large extent on the skeletons of adult animals, of the knowledge of which he was a master. As in the course of development modifications in shape and in the relative position of parts not unfrequently occur, and their original character and place of origin become obscured, it is difficult, from the study only of adults, to arrive at a correct interpretation of their morphological significance. When the changes which take place in the skull during its development, as worked out by Reichert and Rathke, became known and their value had become appreciated, many of the conclusions arrived at by Owen were challenged and ceased to be accepted. It is, however, due to that eminent anatomist to state, from my personal knowledge of the condition of anatomical science in this country fifty years ago, that an enormous impulse was given to the study of comparative morphology by his writings, and by the criticisms to which they were subjected.

There can be no doubt that generalised arrangements do exist in the early embryo which, up to a certain stage, are common to animals that in their adult condition present diverse characters and out of which the forms special to different groups are evolved. As an illustration of this principle, I may refer to the stages of development of the great arteries in the bodies of vertebrate animals. Originally, as the observations of Rathke have taught us, the main arteries are represented by pairs of symmetrically arranged vascular arches, some of which enlarge and constitute the permanent arteries in the adult, whilst others disappear. The increase in size of some of these arches, and the atrophy of others, are so constant for different groups that they constitute anatomical features as distinctive as the modifications in the skeleton itself. Thus in mammals the fourth vascular arch on the left side persists, and forms the arch of the aorta; in birds the corresponding part of the aorta is an enlargement of the fourth right arch, and in reptiles both arches persist to form the great artery. That this original symmetry exists also in man we know from the fact that now and

again his body, instead of corresponding with the mammalian type, has an aortic arch like that which is natural to the bird, and in rarer cases even to the reptile. A type form common to the vertebrata does therefore in such cases exist, capable of evolution in more than one direction.

The reputation of Thomas Henry Huxley as a philosophic comparative anatomist rests largely on his early perception of, and insistence on, the necessity of testing morphological conclusions by a reference to the development of parts and organs, and by applying this principle in his own investigations. The principle is now so generally accepted by both botanists and anatomists that morphological definitions are regarded as depending essentially on the successive phases of the development of the parts under consideration.

The morphological characters exhibited by a plant or animal tend to be hereditarily transmitted from parents to offspring, and the species is perpetuated. In each species the evolution of an individual, through the developmental changes in the egg, follows the same lines in all the individuals of the same species, which possess therefore in common the features called specific characters. The transmission of these characters is due, according to the theory of Weismann, to certain properties possessed by the chromosome constituents of the segmentation nucleus in the fertilised ovum, named by him the germ-plasm, which is continued from one generation to another, and impresses its specific character on the egg and on the plant or animal developed from it.

As has already been stated, the special tissues which build up the bodies of the more complex organisms are evolved out of cells which are at first simple in form and appearance. During the evolution of the individual, cells become modified or differentiated in structure and function, and so long as the differentiation follows certain prescribed lines the morphological characters of the species are preserved. We can readily conceive that, as the process of specialisation is going on, modifications or variations in groups of cells and the tissues derived from them, notwithstanding the influence of heredity, may in an individual diverge so far from that which is characteristic of the species as to assume the arrangements found in another species, or even in another order. Anatomists had indeed long recognised that variations from the customary arrangement of parts occasionally appeared, and they described such deviations from the current descriptions as irregularities.

Darwinian Theory.

The significance of the variations which arise in plants and animals had not been apprehended until a flood of light was thrown on the entire subject by the genius of Charles Darwin, who formulated the wide-reaching theory that variations could be transmitted by heredity to younger generations. In this manner he conceived new characters would arise, accumulate, and be perpetuated, which would in the course of time assume specific importance. New species might thus be evolved out of organisms originally distinct from them, and their specific characters would in turn be transmitted to their descendants. By a continuance of this process new species would multiply in many directions, until at length from one or more originally simple forms the earth would become peopled by the infinite varieties of plant and animal organisms which have in past ages inhabited, or do at present inhabit, our globe. The Darwinian theory may therefore be defined as Heredity modified and influenced by Variability. It assumes that there is an hereditary quality in the egg which, if we take the common fowl for an example, shall continue to produce similar fowls. Under conditions, of which we are ignorant, which occasion molecular changes in the cells and tissues of the developing egg, variations might arise in the first instance probably slight, but becoming intensified in successive generations, until at length the descendants would have lost the characters of the fowl and have become another species. No precise

estimate has been arrived at, and indeed one does not see how it is possible to obtain it, of the length of years which might be required to convert a variation, capable of being transmitted, into a new and definite specific character.

The circumstances which, according to the Darwinian theory, determined the perpetuation by hereditary transmission of a variety and its assumption of a specific character, depended, it was argued, on whether it possessed such properties as enabled the plant or animal in which it appeared to adapt itself more readily to its environment, *i. e.*, to the surrounding conditions. If it were to be of use the organism in so far became better adapted to hold its own in the struggle for existence with its fellows and with the forces of nature operating on it. Through the accumulation of useful characters the specific variety was perpetuated by natural selection so long as the conditions were favourable for its existence, and it survived as being the best fitted to live. In the study of the transmission of variations which may arise in the course of development, it should not be too exclusively thought that only those variations are likely to be preserved which can be of service during the life of the individual, or in the perpetuation of the species, and possibly available for the evolution of new species. It should also be kept in mind that morphological characters can be transmitted by hereditary descent, which, though doubtless of service in some bygone ancestor, are, in the new conditions of life of the species, of no physiological value. Our knowledge of the structural and functional modifications to be found in the human body, in connection with abnormalities and with tendencies or pre-disposition to diseases of various kinds, teaches us that characters which are of no use, and indeed detrimental to the individual, may be hereditarily transmitted from parents to offspring through a succession of generations.

Since the conception of the possibility of the evolution of new species from pre-existing forms took possession of the minds of naturalists, attempts have been made to trace out the lines on which it has proceeded. The first to give a systematic account of what he conceived to be the order of succession in the evolution of animals was Ernst Haeckel, of Jena, in a well-known treatise. Memoirs on special departments of the subject, too numerous to particularise, have subsequently appeared. The problem has been attacked along two different lines; the one by embryologists, of whom may be named Kowalewsky, Gegenbaur, Dohrn, Ray Lankester, Balfour, and Gaskell, who with many others have conducted careful and methodical inquiries into the stages of development of numerous forms belonging to the two great divisions of the animal kingdom. Invertebrates, as well as vertebrates, have been carefully compared with each other in the bearing of their development and structure on their affinities and descent, and the possible sequence in the evolution of the Vertebrata from the Invertebrata has been discussed. The other method pursued by palæontologists, of whom Huxley, Marsh, Cope, Osborne, and Traquair are prominent authorities, has been the study of the extinct forms preserved in the rocks, and the comparison of their structure with each other and with that of existing organisms. In the attempts to trace the line of descent the imagination has not unfrequently been called into play in constructing various conflicting hypotheses. Though from the nature of things the order of descent is, and without doubt will continue to be, ever a matter of speculation and not of demonstration, the study of the subject has been a valuable intellectual exercise and a powerful stimulant to research.

We know not as regards time when the fiat went forth, "Let there be Life, and there was Life." All we can say is that it must have been in the far-distant past, at a period so remote from the present that the mind fails to grasp the duration of the interval. Prior to its genesis our earth consisted of barren rock and desolate ocean. When

matter became endowed with Life, with the capacity of self-maintenance and of resisting external disintegrating forces, the face of nature began to undergo a momentous change. Living organisms multiplied, the land became covered with vegetation, and multitudinous varieties of plants—from the humble fungus and moss to the stately palm and oak—beautified its surface and fitted it to sustain higher kinds of living beings. Animal forms appeared, in the first instance simple in structure, to be followed by others more complex, until the mammalian type was produced. The ocean also became peopled with plant and animal organisms, from the microscopic diatom to the huge leviathan. Plants and animals acted and reacted on each other, on the atmosphere which surrounded them, and on the earth on which they dwelt, the surface of which became modified in character and aspect. At last Man came into existence. His nerve-energy, in addition to regulating the processes in his economy which he possesses in common with animals, was endowed with higher powers. When translated into psychical activity it has enabled him throughout the ages to progress from the condition of a rude savage to an advanced stage of civilisation; to produce works in literature, art, and the moral sciences, which have exerted, and must continue to exert, a lasting influence on the development of his higher Being; to make discoveries in physical science; to acquire a knowledge of the structure of the earth, of the ocean in its changing aspects, of the atmosphere and the stellar universe, of the chemical composition and physical properties of matter in its various forms, and to analyse, comprehend, and subdue the forces of nature.

By the application of these discoveries to his own purposes Man has, to a large extent, overcome time and space; he has subdued the ocean with steamships, girdled the earth with the electric wire, tunneled the lofty Alps, spanned the Forth with a bridge of steel, invented machines and founded industries of all kinds for the promotion of his material welfare, elaborated systems of government fitted for the management of great communities, formulated economic principles, obtained an insight into the laws of health, the causes of infective diseases, and the means of controlling and preventing them.

When we reflect that many of the most important discoveries in abstract science and in its applications have been made during the present century, and indeed since the British Association held its first meeting in the ancient capital of your county sixty-nine years ago, we may look forward with confidence to the future. Every advance in science provides a fresh platform from which a new start can be made. The human intellect is still in process of evolution. The power of application and of concentration of thought for the elucidation of scientific problems is by no means exhausted. In science is no hereditary aristocracy. The army of workers is recruited from all classes. The natural ambition of even the private in the ranks to maintain and increase the reputation of the branch of knowledge which he cultivates affords an ample guarantee that the march of science is ever onwards, and justifies us in proclaiming for the next century, as in the one fast ebbing to a close, that Great is Science, and it will prevail.

New Work on Gas Lighting.—Messrs. J. and A. Churchill announce the issue of Vol. III. of "Chemical Technology, or Chemistry in its Applications to Arts and Manufactures," edited by Charles Edward Groves, F.R.S., and William Thorp, B.Sc. This volume is on "Gas Lighting," by Charles Hunt, manager of the Birmingham Corporation Gas Works. It is expected that the work will attract the attention of all interested in the disputed subject of the advantages of gas and electric lighting. Coal of course comes under consideration.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 7, August 13, 1900.

Action of Hydrogen on the Arsenic Sulphides.—H. Pélabon.—Hydrogen, when acting on sulphides of arsenic at temperatures above 300°, produces sulphuretted hydrogen. Inversely, sulphuretted hydrogen attacks arsenic within the same limits of temperature. The author investigates these two inverse reactions. The realgar and hydrogen were kept in sealed tubes at a given temperature of 610° for periods of five, ten, twenty, sixty, and one hundred and twenty minutes. The numbers found for the relation of the partial pressure of the hydrogen sulphide to the total pressure of mixed gases in the tube show the existence of a limit to the reaction. Using the same apparatus, the author found that sulphuretted hydrogen attacks arsenic at 610°, the reaction again being limited.

Properties of the Blue Oxide of Molybdenum.—Marcel Guichard.—In a former paper the author described the preparation of the hydrated blue oxide of molybdenum corresponding to the formula $\text{MoO}_2 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$. A study of the properties of this blue oxide shows that it is in reality a molybdate; it only exists in a hydrated state, it being impossible to obtain anhydrous oxide of molybdenum corresponding to the blue hydrated oxide. Considering the results of the series of researches which the author has made on the various molybdenum oxides, he arrives at the following conclusion:—The number of anhydrous oxides of molybdenum, which has been stated as five by various chemists, is, in reality, two only—the anhydrous dioxides, MoO_2 , and the anhydrous trioxide, MoO_3 .

Composition of the Ashes of several Medicinal Plants.—A. B. Griffiths.

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NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 21st. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, 19th September.

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FREDERICK MITCHELL,
Secretary.

49, Windmill Street,
Gravesend.
August 31st, 1900.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2129.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. BRADFORD, 1900.

By Professor W. H. PERKIN, Jun., Ph.D., F.R.S.,
President of the Section.

The Modern System of Teaching Practical Inorganic Chemistry and its Development.

In choosing for the subject of my Address to-day the development of the teaching of practical inorganic chemistry I do so, not only on account of the great importance of the subject, but also because it does not appear that this matter has been brought before this Section, in the President's Address at all events, during the last few years.

In dealing generally with the subject of the teaching of chemistry as a branch of science, it may be well in the first place to consider the value of such teaching as a means of general education, and to turn our attention for a few minutes to the development of the teaching of science in schools.

There can be no doubt that there has been great progress in the teaching of science in schools during the last forty years, and this is very evident from the perusal of the essay, entitled "Education: Intellectual, Moral, and Physical," which Herbert Spencer wrote in 1859. After giving his reasons for considering the study of science of primary importance in education, Herbert Spencer continues: "While what we call civilisation could never have arisen had it not been for science, science forms scarcely an appreciable element in our so-called civilised training."

From this it is apparent that science was not taught to any appreciable extent in schools at that date, though, doubtless, in some few schools occasional lectures were given on such scientific subjects as physiology, anatomy, astronomy, and mechanics.

Herbert Spencer's pamphlet appears to have had only a very gradual effect towards the introduction of science into schemes of education. For many years chemical instruction was only given in schools at the schoolroom desk, or at the best from the lecture table, and many of the most modern of schools had no laboratories.

The first school to give any practical instruction in chemistry was apparently the City of London School, at which, in the year 1847, Mr. Hall was appointed teacher of chemistry, and there he continued to teach until 1869.* Besides the lecture theatre and a room for storing apparatus, Mr. Hall's department contained a long room, or rather passage, leading into the lecture theatre, and closed at each end with glass doors. In this room, which was fitted up as a laboratory, and used principally as a preparation room for the lectures, Mr. Hall performed experiments with the few boys who assisted him with his lectures. As accommodation was at that time strictly limited, he used to suggest simple experiments, and encourage the boys to carry them out at home, and afterwards he himself would examine the substances which they had made.

From this small beginning the teaching of chemistry in the City of London School rapidly developed, and this school now possesses laboratories which compare favourably with those of any school in the country.

The Manchester Grammar School appears to have been one of the first to teach practical chemistry. In connection with this school a small laboratory was built in 1868; this was replaced by a larger one in 1872, and the present large laboratories, under the charge of Mr. Francis Jones, were opened in 1880.

Dr. Marshall Watts, who was the first science master in this school, taught practical chemistry along with the theoretical work from the commencement in 1868.

As laboratories were gradually multiplied, it might be supposed that boys were given the opportunity to carry out experiments which had a close connection with their lecture-room courses. But the programme of laboratory work which became all but universal was the preparation of a few gases, followed by the practice of qualitative analysis. The course adopted seems to have been largely built up on the best books of practical chemistry in use in the colleges at that time; but it was also, no doubt, largely influenced by the requirements of the syllabus of the Science and Art Department, which contained a scheme for teaching practical chemistry.* Even down to quite recent times it was in many schools still not considered essential that boys should have practical instruction in connection with lectures in chemistry.

A Report issued in 1897 by a special Committee appointed by the Technical Education Board of the London County Council, adduces evidence of this from twenty-five secondary schools in London, in which there were 3960 boys learning chemistry. Of these 1698 boys, or 43 per cent, did no practical work whatever; 955 boys, or 24 per cent, did practical work, consisting of a certain amount of preparation of gases, together with qualitative analysis; but of these latter 743, or 77 per cent, had not reached the study of the metals in their theoretical work, so that their testing work can have been of little educational value. It was also found that in the case of 655, or 68 per cent of the total number of boys taking practical work, the first introduction to practical chemistry was through qualitative analysis.

But some years before this Report was issued, a movement had begun which was destined to have a far-reaching effect. A Report "on the best means for promoting Scientific Education in Schools" having been presented to the Dundee Meeting of this Association in 1867, and published in 1868, a Committee of the British Association was appointed in 1887 "for the purpose of inquiring and reporting upon the present methods of teaching chemistry." The well-known Report which this Committee presented to the Newcastle Meeting in 1889 insisted that it was worth while to teach chemistry in schools, not so much for the usefulness of the information imparted, as for the special mental discipline it afforded if the scientific method of investigating nature were employed. It was argued that "learners should be put in the attitude of discoverers, and led to make observations, experiments, and inferences for themselves." And since there can be little progress without measurement, it was pointed out that the experimental work would necessarily be largely of a quantitative character.

Professor H. E. Armstrong, in a paper read at a conference at the Health Exhibition five years before this, had foreshadowed much that was in this Report. He also drew up a detailed scheme for "a course of elementary instruction in physical science," which was included in the Report of the Committee, and it cannot be doubted that this scheme and the labours of the Committee have had a very marked influence on the development of the teaching of practical chemistry in schools. That this in-

* Mr. A. T. Pollard, M.A., Head Master of the City of London School, has kindly instituted a search among the bound copies of the boys' terminal reports, and informs me that in the School form of Terminal Report a heading for Chemistry was introduced in the year 1847, the year of Mr. Hall's appointment.

* I find, on inquiry, that examinations in the Advanced Stage and Honours of Practical Chemistry were first held by the Science and Art Department in 1878, the practical examination being extended to the Elementary Stage in 1882.

fluence has been great will be admitted when it is understood that schemes based on the recommendation of the Committee are now included in the codes for both Elementary Day Schools and Evening Continuation Schools. The recent syllabuses for elementary and advanced courses issued by the Incorporated Association of Headmasters, and by the Oxford and Cambridge local boards and others, are evidently directly inspired by the ideas set forth by the Committee.

The Department of Science and Art has also adopted some of the suggestions of the Committee, and a revised syllabus was issued by the Department in 1895, in which qualitative analysis is replaced by quantitative experiments of a simple form, and by other exercises so framed "as to prevent answers being given by students who have obtained their information from books or oral instruction." This was a very considerable advance, but it must be admitted that there is nothing in the syllabus which encourages, or even suggests, placing the learners in the attitude of discoverers, and this, in the opinion of the Committee of this Association, is vital if the teaching is to have educational value.

Many criticisms have been passed upon the 1889 Report. It has been said that life is much too short to allow of each individual advancing from the known to the unknown, according to scientific methods, and that even were this not so too severe a tax is made upon the powers of boys and girls. In answer to the second point it will be conceded that while it is doubtless futile to try to teach chemistry to young children, on the other hand experience has abundantly shown that the average schoolboy of fourteen or fifteen can, with much success, investigate such problems as were studied in the researches of Black and Scheele, of Priestley and Cavendish, and Lavoisier, and it is quite remarkable with what interest such young students carry out this class of work.

It may be well to quote the words which Sir Michael Foster used in this connection in his admirable Presidential Address to this Association in 1899. He said:—"The learner may be led to old truths, even the oldest, in more ways than one. He may be brought abruptly to a truth in its finished form, coming straight to it like a thief climbing over a wall; and the hurry and press of modern life tempt many to adopt this quicker way. Or he may be more slowly guided along the path by which the truth was reached by him who first laid hold of it. It is by this latter way of learning the truth, and by this alone, that the learner may hope to catch something at least of the spirit of the scientific inquirer."

I believe that in the determination of a suitable school course in experimental science this principle of historical development is a very valuable guide, although it is not laid down in the 1889 Report of the British Association.

The application of this principle will lead to the study of the solvent action of water, of crystallisation, and of the separation of mixtures of solids before the investigation of the composition of water, and also before the investigation of the phenomena of combustion. It will lead to the investigation of hydrochloric acid before chlorine, and especially to the postponement of atomic and molecular theories, chemical equations, and the laws of chemical combination, until the student has really sufficient knowledge to understand how these theories came to be necessary.

There can be no doubt that this new system of teaching chemistry in schools has been most successful. Teachers are delighted with the results which have already been obtained, and those whom I have had the opportunity of consulting, directly and indirectly, cannot speak too highly of their satisfaction at the disappearance of the old system of qualitative analysis, and the institution of the new order of things. Especially I may mention in this connection the excellent work which is being carried on under the supervision of Dr. Bevan Lean at the Friends' School in Ackworth, where the boys have attained re-

sults which are far in advance of anything which would have been thought possible a few years since.

It is, of course, obvious that if a schoolboy is made to take the attitude of a discoverer his progress may appear to be slow. But does this matter? Most boys will not become professional chemists; but if while at school a boy learns how to learn, and how to "make knowledge" (cf. Professor J. G. Macgregor in *Nature*, September, 1899) by working out for himself a few problems, a habit of mind will be formed which will enable him in future years to look in a scientific spirit at any new problems which may face him. When school days are past the details of the preparation of hydrogen may have been forgotten; but if it was really understood at the time that it could not be decided at once whether the gas was derived from the acid or from the metal, or from the water, or in part from the one and in part from the other, an attitude of scepticism and of suspended judgment will have been formed, which will continue to guard from error.

In the new system of teaching chemistry in schools much attention must necessarily be given to weights and measurements; indeed, the work must be largely of a quantitative kind, and it is in this connection that an important note of warning has been sounded by several teachers (cf. H. Piñon in *The School World*, November, 1899; Bevan Lean, *ibid.*, February, 1890). They consider, very rightly, that it is important to point out clearly to the scholar that science does not consist of measurement, but that measurement is only a tool in the hand of the inquirer, and that when once sufficient skill has been developed in its use it should be employed only with a distinct object. Measurements should, in fact, be made only in reference to some actual problem which appears to be really worth solving, not in the accumulation of aimless details.

And, of course, all research carried out must be genuine and not sham, and all assumption of the "obvious" must be most carefully guarded against. But the young scholar must, at the same time, not forget that although the scientific method is necessary to enable him to arrive at a result, in real life it is the answer to the problem which is of the most importance (cf. Mrs. Bryant, *Special Reports on Educational Subjects*, vol. ii., p. 113).

Although, then, there has been so much discussion, during the last ten years, on the subject of teaching chemistry in schools, and such steady progress has been made towards devising a really satisfactory system of teaching the subject to young boys and girls, it is certainly very remarkable that practically nothing has been said or written bearing on the training which a student, who wishes to become a chemist, is to undertake at the close of his school days at the college or university in which his education is continued.

One of the most remarkable points, to my mind, in connection with the teaching of chemistry, is the fact that although the science has been advancing year by year with such unexampled rapidity, the course of training which the student goes through during his first two years at most colleges is still practically the same as it was thirty or forty years ago. Then, as now, after preparing a few of the principal gases, the student devotes the bulk of his first year to qualitative analysis in the dry and wet way, and his second year to quantitative analysis, and, although the methods employed in teaching the latter may possibly have undergone some slight modification, there is certainly no great difference between the routine of simple salt and mixture, followed by quantitative analysis practised at the present day, and that which was in vogue in the days of our fathers and grandfathers.

Since, then, the present system has held the field for so long, not only in this country but also on the Continent, it is worth while considering whether it affords the best training which a student who wishes to become a chemist can undergo in the short time during which he can attend at a college or university. In considering this matter I was led in the first place to carefully examine old books

and other records, with the object of finding out how the present system originated, and I think that valuable and interesting information bearing on the subject may be obtained from a very brief sketch of the rise and development of the present system of teaching chemistry, and especially in so far as it bears on the inclusion of qualitative analysis. Unfortunately, it is not so easy to gain a good historical acquaintance with the matter as I at first imagined would be the case, and this is due in a large measure to the fact that so few of the laboratories which took an active part in the development of the present system of chemical training have left any record of the methods which they employed. In this connection I may perhaps be allowed to suggest that it would be a valuable help to the future historian if all prominent teachers of chemistry would leave behind them a brief record of the system of teaching adopted in their laboratories, showing the changes which they had instituted, the object of these changes, and the results which followed their adoption.

There is no doubt that the progress of practical chemistry went largely hand in hand with the progress of theoretical chemistry, for as the latter gradually developed, so the necessity for the determination of the composition, first of the best known, and then of the rarer minerals and other substances, became more and more marked.

The analytical examination of substances in the dry way was employed in very early times in connection with metallurgical operations, and especially in the determination of the presence of valuable constituents in samples of minerals. Cupellation was used by the Greeks in the separation of gold and silver from their ores and in the purification of these metals. Geber knew that the addition of nitre to the ore facilitated the separation of gold and silver, and subsequently Glauber (1604-1668) called attention to the fact that many commoner metals could easily be separated from their ores with the aid of nitre.

But it was not till the eighteenth century that any marked progress was made in analysis in the dry way, and the progress which then became rapid was undoubtedly due to the discovery of the blowpipe, and to the introduction of its use into analytical operations. The blowpipe is mentioned for the first time in 1660, in the Transactions of the Accademia del Cimento of Florence, but the first to recommend its use in chemical operations was Johann Andreas Cramer in 1739. The progress of blowpipe analysis was largely due to Gahn (1745-1818), who spent much time in perfecting its use in the examination of minerals, and it was he who first used platinum wire and cobalt solution in connection with blowpipe analysis. The methods employed by Gahn were further developed by his friend Berzelius (1779-1848), who gave much attention to the matter, and who with great skill and patience gradually worked out a complete scheme of blowpipe analysis, and published it in a pamphlet entitled "Ueber die Anwendung des Löthrohrs," which appeared in 1820. After the publication of this work blowpipe analysis rapidly came into general use in England, France, and Germany, and the scheme devised by Berzelius is essentially that employed at the present day.

Indeed, the only notable additions to the methods of analysis in the dry way since the time of Berzelius are the development of flame reactions, which Bunsen worked out with such characteristic skill and ingenuity, and the introduction of the spectroscope.

The necessity for some process other than that of analysis in the dry way seems, in the first instance, to have arisen in quite early times in connection with the examination of drugs, not only on account of the necessity for discovering their constituents, but also as a means of determining whether they were adulterated. In such cases analysis in the dry way was obviously unsuitable, and experience soon showed that the only way to arrive at the desired result was to treat the substance under

examination with aqueous solutions of definite substances, the first reagent apparently being a decoction of gallnuts, which is described by Pliny as being employed in detecting adulteration with green vitriol.

The progress made in connection with wet analysis was, however, exceedingly slow, largely owing to the lack of reagents; but as these were gradually discovered wet analysis rapidly developed, especially in the hands of Tachenius, Scheele, Boyle, Hoffman, Margraf, and Bergmann. Boyle (1626-1691) especially had an extensive knowledge of reagents and their application; and, indeed, it was Boyle who first introduced the word "analysis" for those operations by which substances may be recognised in the presence of one another. Boyle knew how to test for silver with hydrochloric acid, for calcium salts with sulphuric acid, and for copper by the blue solution produced by ammonia.

Margraf (1709-1782) introduced prussiate of potash for the detection of iron, and Bergmann (1735-1784) not only introduced new reagents and new methods for decomposing minerals and refractory substances, such as fusion with potash, digestion with nitric acid or hydrochloric acid, but he also was the first to suggest the application of tests in a systematic way, and, indeed, the method of analysis which he developed is on much the same lines as that in use at the present day. He paid special attention to the qualitative analysis of minerals, and gave careful instructions for the analysis of gold, platinum, silver, lead, copper, zinc, and other ores. The work of Scheele (1742-1786) had indirectly a great influence on qualitative analysis, as, although he did not give a general systematic method of procedure in the analysis of substances of unknown composition, yet the methods which he employed in the examination of new substances were so original and exact as to remain models of how qualitative analysis should be conducted.

Great strides in analytical chemistry in the wet way were made through the work of Berzelius, who, by the discovery of new methods, such as the decomposition of silicates by hydrofluoric acid and the introduction of new tests, greatly advanced the art. He paid special attention to perfecting the methods of analysis of mineral waters, and these researches as well as his work on ores, and particularly his investigation of platinum ores, stamp Berzelius as one of the great pioneers in qualitative and quantitative analytical chemistry.

By the labours of the great experimenters whom I have mentioned qualitative analysis gradually acquired the familiar appearance of to-day, and many books were written with the object of arranging the mass of information which had accumulated, and of thus rendering it available for the student in his efforts to investigate the composition of new minerals and other substances. Among these books may be mentioned the "Handbuch der Analytischen Chemie," by H. Rose, and especially the well-known analytical text-books of Fresenius, which have had an extraordinarily wide circulation and passed through many editions.

The work of the great pioneers in analytical chemistry was work done often under circumstances of great difficulty, as before the end of the seventeenth century there were no public institutions of any sort in which a practical knowledge of chemistry could be acquired. Lectures were, of course, given from very early times, but it was not until the time of Guillaume François Rouelle (1703-1770), at the beginning of the eighteenth century, that lectures began to be illustrated by experiments. Rouelle, who was very active as a teacher, numbered among his pupils many men of eminence, such as Lavoisier and Proust, and it was largely owing to his influence that France took such a lead in practical teaching. In Germany progress was much slower, and in our country the introduction of lectures illustrated by experiments seems to have been mainly due to Davy.

When it is considered how slowly experimental work came to be recognised as a means of illustration and

education, even in connection with lectures, it is not surprising that in early times practical teaching in laboratories should have been thought quite unnecessary.

The few laboratories which existed in the sixteenth century were built mainly for the practice of alchemy by the reigning princes of the time, and, indeed up to the beginning of the nineteenth century, the private laboratories of the great masters were the only schools in which a favoured few might study, but which were not open to the public. Thus we find that Berzelius received in his laboratory a limited number of students who worked mostly at research: these were not usually young men, and his school cannot thus be considered as a teaching institution in the ordinary sense of the word.

The earliest laboratory open for general instruction in Great Britain was that of Thomas Thomson, who, after graduating in Edinburgh in 1799, began lecturing in that city in 1800, and opened a laboratory for the practical instruction of his pupils. Thomson was appointed Lecturer in Chemistry in Glasgow University in 1807, and Regius Professor in 1818, and in Glasgow he also opened a general laboratory.

The first really great advance in laboratory teaching is due to Liebig, who, after working for some years in Paris under Gay-Lussac, was appointed in 1824 to be Professor of Chemistry in Giessen. Liebig was strongly impressed with the necessity for public institutions where any student could study chemistry, and to him fell the honour of founding the world-famed Giessen Laboratory, the first public institution in Germany which brought practical chemistry within the reach of all students.

Giessen rapidly became the centre of chemical interest in Germany, and students flocked to the laboratory in such numbers as to necessitate the development of a systematic course of practical chemistry, and in this way a scheme of teaching was devised which, as we shall see later, has served as the foundation for the system of practical chemistry in use at the present day.

When the success of this laboratory had been clearly established many other towns discovered the necessity for similar institutions, and in a comparatively short time every university in Germany possessed a chemical laboratory. The teaching of practical chemistry in other countries was, however, of very slow growth; in France, for example, Wurtz in 1869 drew attention to the fact that there was at that time only one laboratory which could compare with the German laboratories, namely, that of the Ecole Normale Supérieure.

In this country the provision of suitable laboratories for the study of chemistry seems to date from the year 1845, when the College of Chemistry was founded in London, an institution which under A. W. Hofmann's guidance rapidly rose to such a prominent position.

In 1851 Frankland was appointed to the chair of chemistry in the new college founded in Manchester by the trustees of John Owens, and here he equipped a laboratory for the teaching of practical chemistry. Under Sir Henry Roscoe this laboratory soon became too small for the growing number of chemical students, a defect which was removed when the new buildings of the college were opened in 1873. In 1849 Alexander Williamson was appointed Professor of Practical Chemistry at University College, London, where he introduced the practical methods of Liebig.

Following these examples, the older universities gradually came to see the necessity for providing accommodation for the practical teaching of chemistry, with the result that well-equipped laboratories have been erected in all the centres of learning in this country.

Since Liebig, by the establishment of the Giessen Laboratory, must be looked upon as the pioneer in the development of practical laboratory teaching, it will be interesting to endeavour to obtain some idea of the methods which he used in the training of the students who attended his laboratory in Giessen. From small beginnings he gradually introduced a systematic course of practical

chemistry, and a careful comparison shows that this was similar in many ways to that in use at the present day. The student at Giessen, after preparing the more important gases, was carefully trained in qualitative and quantitative analysis; he was then required to make a large number of preparations, after which he engaged in original research.

Although there is, as far as I have been able to ascertain, no printed record of the nature of the quantitative work and the preparations which Liebig required from his students, the course of qualitative analysis is easily followed, owing to the existence of a most interesting book published for the use of the Giessen students.

In 1846, at Liebig's request, Henry Will, Ph.D., Extraordinary Professor of Chemistry in the University of Giessen, wrote a small book, for use at Giessen, called "Giessen Outlines of Analysis," which shows clearly the kind of instruction given in that laboratory at the time in so far as qualitative analysis is concerned. This book, which contains a preface by Liebig, is particularly interesting on account of the fact that it is evidently the first Introduction to Analysis intended for the training of elementary students which was ever published. In the preface Liebig writes:—"The want of an introduction to chemical analysis adapted for the use of a laboratory has given rise to the present work, which contains an accurate description of the course I have followed in my laboratory with great advantage for twenty-five years. It has been prepared at my request by Professor Will, who has been my assistant during a great part of this period."

This book undoubtedly had a considerable circulation, and was used in most of the laboratories which were in existence at that time, and thus we find, for example, that the English translation, which Liebig "hopes and believes will be acceptable to the English public" was the book used by Hofmann for his students at the College of Chemistry. In this book the metals are first divided into groups much in the same way as is done now; each group is then separately dealt with, the principal characteristics of the metals of the group are noted, and their reactions studied. Those tests which are useful in the detection of each metal are particularly emphasised, and the reasons given for selecting certain of them as of special value for the purposes of separating one metal from another.

Throughout this section of the book there are frequent discussions as to the possible methods of the separation, not only of the metals of one group, but of those belonging to different groups; and the whole subject is treated in a manner which shows clearly that Liebig's great object was to make the student think for himself. After studying in a similar manner the behaviour of the principal acids with reagents, the student is introduced to a course of qualitative analysis comprising, 1, preliminary examination of solids; 2, qualitative analysis of the substance in solution.

Both sections are evidently written with the object, not only of constructing a system of qualitative analysis, but more particularly of clearly leading the student to argue out for himself the methods of separation which he will ultimately adopt. The book concludes with a few tables, which differ considerably in design from those in use at the present day, and which are so meagre that the student could not possibly have used them mechanically.

The system introduced in this book, no doubt owing to the excellent results obtained by its use, was rapidly recognised as the standard method of teaching analysis in most of the institutions existing at that time. Soon the course began to be further developed, book after book was published on the subject, and gradually the teaching of qualitative analysis assumed the shape and form with which we are all so well acquainted. But the present-day book on qualitative analysis differs widely from "Giessen Outlines" in this respect, that whereas in the latter the tables introduced are mere indications of the methods of separation to be employed, and are of such a nature that the student who did not think for himself must have been constantly in difficulties, in the book of the present day

these tables have been worked out to the minutest detail. Every contingency is provided for; nothing is left to the originality of the student; and that which, no doubt, was once an excellent course has now become so hopelessly mechanical as to make it doubtful whether it retains anything of its former educational value.

The question which I now wish to consider more particularly is whether the system of training chemists which is at present adopted, with little variation, in our colleges and universities, is a really satisfactory one, and whether it supplies the student with the kind of knowledge which will be of the most value to him in his future career.

Those who study chemistry may be roughly divided as to their future careers into two groups—those who become teachers and those who become technical chemists. Now, whether the student takes up either the one or the other career, I think that it is clear that the objects to be aimed at in training him are to give him a sound knowledge of his subject, and especially to so arrange his studies as to bring out in every possible way his capacity for original thought.

A teacher who has no originality will hardly be successful, even though he may possess a very wide knowledge of what has already been done in the past. He will have little enthusiasm for his subject, and will continue to teach on the lines laid down by the text-books of the day, without himself materially improving the existing methods, and, above all, he will be unable, and will have no desire, to add to our store of knowledge by original investigation.

It is in the power of almost every teacher to do some research work, and it seems probable that the reason why more is not done by teachers is because the importance of research work was not sufficiently insisted on, and their original faculty was not sufficiently trained, at the schools and colleges where they received their education.

And these remarks apply with equal force to the student who subsequently becomes a technical chemist.

In the chemical works of to-day sound knowledge is essential, but originality is an even more important matter. A technical chemist without originality can scarcely rise to a responsible position in a large works, whereas a chemist who is capable of constantly improving the processes in operation, and of adding new methods to those in use, becomes so valuable that he can command his own terms.

Now, this being so, I think it is extraordinary that so many of the students who go through the prescribed course of training—say for the Bachelor of Science degree—not only show no originality themselves, but seem also to have no desire at the conclusion of their studies to engage in original investigation under the supervision of the teacher. That this is so is certainly my experience as a teacher examiner, and I feel sure that many other teachers will endorse this view of the case.

If we inquire into the reason for this deficiency in originality we shall, I think, be forced to conclude that it is in a large measure due to the conditions of study and the nature of the courses through which the student is obliged to pass.

A well-devised system of quantitative analysis is undoubtedly valuable in teaching the student accurate manipulation, but it has always seemed to me that the long course of qualitative analysis, which is usually considered necessary, and which generally precedes the quantitative work, is not the most satisfactory training for a student.

There can be no doubt that to many students qualitative analysis is little more than a mechanical exercise; the tables of separation are learnt by heart, and every substance is treated in precisely the same manner; such a course is surely not calculated to develop any original faculty which the student may possess. Then, again, when the student passes on to quantitative analysis, he receives elaborate instructions as to the little details he must observe in order to get an accurate result; and even after he has become familiar with the simpler determin-

ations he rarely attempts, and indeed has no time to attempt, anything of the nature of an original investigation in qualitative or quantitative analysis. It indeed sometimes happens that a student at the end of his second year has never prepared a pure substance, and is often utterly ignorant of the methods employed in the separation of substances by crystallisation; he has never conducted a distillation, and has no idea how to investigate the nature and amounts of substances formed in chemical reactions; practically all his time has been taken up with analysis. That this is not the way to teach chemistry was certainly the opinion of Liebig, and in support of this I quote a paragraph bearing on the subject, which occurs in a very interesting book on "Justus von Liebig: his Life and Work," written by W. A. Shenstone (pp. 175, 176).

"In his practical teaching Liebig laid great stress on the producing of chemical preparations; on the students preparing, that is to say, pure substances in good quantity from crude materials. The importance of this was, even in Liebig's time, often overlooked; and it was, he tells us, more common to find a man who could make a good analysis than to find one who could produce a pure preparation in the most judicious way."

"There is no better way of making one's self acquainted with the properties of a substance than by first producing it from the raw material, then converting it into its compounds, and so becoming acquainted with them. By the study of ordinary analysis one does not learn how to use the important methods of crystallisation, fractional distillation, nor acquire any considerable experience in the proper use of solvents. In short, one does not, as Liebig said, become a chemist."

One reason why the present system of training chemists has persisted so long is, no doubt, because it is a very convenient system; it is easily taught, does not require expensive apparatus, and, above all, it lends itself admirably for the purpose of competitive examination.

The system of examination which has been developed during the last twenty years has done much harm, and is a source of great difficulty to any conscientious teacher who is possessed of originality, and is desirous, particularly in special cases, of leaving the beaten track.

In our colleges and universities most of the students work for some definite examination—frequently for the Bachelor of Science degree—either at their own University or at the University of London.

For such degrees a perfectly definite course is prescribed and must be followed, because the questions which the candidate will have to answer at his examination are based on a syllabus, which is either published or is known by precedent to be required. The course which the teacher is obliged to teach is thus placed beyond his individual power of alteration, except in minor details, and originality in the teacher is thereby discouraged; he knows that all students must face the same examination, and he must urge the backward man through exactly the same course as his more talented neighbour.

In almost all examinations salts or mixtures of salts are given for qualitative analysis. "Determine the constituents of the simple salt A and of the mixture B" is a favourite examination formula; and as some practical work of this sort is sure to be set, the teacher knows that he must contrive to get one and all of his students into a condition to enable them to answer such questions.

If, then, one considers the great amount of work which is required from the present-day student, it is not surprising that every aid to rapid preparation for examination should be accepted with delight by the teacher; and thus it comes about that tables are elaborated in every detail, not only for qualitative analysis in inorganic chemistry, but, what is far worse, for the detection of some arbitrary selection of organic substances which may be set in the syllabus for examination. I question whether any really competent teacher will be found to recommend this system as one of educational value, or calculated to

bring out and train the faculty of original thought in students.

If, then, the present system is so unsatisfactory, it will naturally be asked, How are students to be trained, and how are they to be examined, so as to find out the extent of the knowledge of their subject which they have acquired?

In dealing with the first part of the question—that is, the training best suited to chemists—I can, of course, only give my own views on the subject—views which, no doubt, may differ much from those of many of the teachers present at this meeting. The objects to be attained are, in my opinion, to give the student a sufficient knowledge of the broad facts of chemistry, and at the same time so to arrange his practical work in particular as to always have in view the training of his faculty of original thought.

I think it will be conceded that any student, if he is to make his mark in chemistry by original work, must ultimately specialise in some branch of the subject. It may be possible for some great minds to do valuable original work in more than one branch of chemistry, but these are the exceptions; and as time goes on, and the mass of facts accumulates, this will become more and more impossible. Now a student at the commencement of his career rarely knows which branch of the subject will fascinate him most, and I think, therefore, that it is necessary, in the first place, to do all that is possible to give him a thorough grounding in all branches of the subject. In my opinion the student is taken over too much ground in the lecture courses of the present day; in inorganic chemistry, for example, the study of the rare metals and their reactions might be dispensed with, as well as many of the more difficult chapters of physical chemistry, and in organic chemistry such complicated problems as the constitutions of uric acid and the members of the camphor and terpene series, &c., might well be left out. As matters stand now, instruction must be given on these subjects simply because questions bearing on them will probably be asked at the examination.

And here perhaps I might make a confession, in which I do not ask my fellow teachers to join me. My name is often attached to chemistry papers which I should be sorry to have to answer, and it seems to me the standard of examination papers, and especially of honours examination papers, is far too high. Should we demand a pitch of knowledge which our own experience tells us cannot be maintained for long?

In dealing with the question of teaching practical chemistry it may be hoped, in the first place, that in the near future a sound training will be given in elementary science in most schools, very much on the lines which I mentioned in the first part of this Address. The student will then be in a fit state to undergo a thoroughly satisfactory course of training in inorganic chemistry during his first two years at college. Without wishing in any way to map out a definite course, I may be allowed to suggest that instead of much of the usual qualitative and quantitative analysis, practical exercises, similar to the following, will be found to be of much greater educational value.

(1). The careful experimental demonstration of the fundamental laws of chemistry and physical chemistry.

(2). The preparation of a series of compounds of the more important metals, either from their more common ores or from the metals themselves. With the aid of the compounds thus prepared the reactions of the different metals might be studied, and the similarities and differences between the different metals then carefully noted.

(3). A course in which the student should investigate in certain selected cases: (a) the conditions under which action takes place; (b) the nature of the products formed; (c) the yield obtained. If he were then to proceed to prepare each product in a state of purity, he would be doing a series of exercises of the highest educational value.

(4). The determination of the combining weights of some of the more important metals. This is, in most cases, comparatively simple, as the determination of the combining weights of selected metals can be very accurately carried out by measuring the hydrogen evolved when an acid acts upon them.

Many other exercises of a similar nature will readily suggest themselves, and in arranging the course every effort should be made to induce the student to consult original papers, and to avoid, as far as possible, any tendency to mere mechanical work.

The exact nature of such a course must, however, necessarily be left very much in the hands of the teacher, and the details will no doubt require much consideration; but I feel sure that a course of practical inorganic chemistry could be constructed which, while teaching all the important facts which it is necessary for the student to know, will, at the same time, constantly tend to develop his faculty of original thought.

Supposing such a course were adopted (and the experiment is well worth trying), there still remains the problem of how the student who has had this kind of training is to be examined.

With regard to his theoretical work there would be no difficulty, as the examination could be conducted on much the same lines as at the present time. In the case of the practical examination, I have long felt that the only satisfactory method of arriving at the value of a student's practical knowledge is by the inspection of the work which he has done during the whole of his course of study, and not by depending on the results of one or two days' set examination. I think that most examiners will agree with me that the present system of examination in practical chemistry is highly unsatisfactory. This is perhaps not so apparent in the case of the qualitative analysis of the usual simple salt or mixture; but when the student has to do a quantitative exercise, or when a problem is set, the results sent in are frequently no indication of the value of the student's practical work. Leaving out of the question the possibility of the student being in indifferent health during the short period of the practical examination, it not infrequently happens that he, in his excitement, has the misfortune to upset a beaker when his quantitative determination is nearly finished, and as a result he loses far more marks than he should do for so simple an accident.

Again, in attacking a problem he has usually only time to try one method of solution, and if this does not yield satisfactory results he again loses marks, whereas in the ordinary course of his practical work, if he were to find that the first method was faulty he would try other methods, until he ultimately arrived at the desired result.

It is difficult to see why such an unsatisfactory system as this might not be replaced by one of inspection, which I think could easily be so arranged as to work well.

A student taking, say, a three years' course for the degree of Bachelor of Science might be required to keep very careful notes of all the practical work which he does during this course, and in order to avoid fraud his notebook could from time to time be initialised by the professor or demonstrator in charge of the laboratory. An inspection of these notebooks could then be made at suitable times by the examiners for the degree, by which means a very good idea would be obtained of the scope of the work which the student had been engaged in, and if thought necessary a few questions could easily be asked in regard to the work so presented. Should the examiners wish to further test the candidate by giving him an examination, I submit that it would be much better to set him some exercise of the nature of a simple original investigation, and to allow him two or three weeks to carry this out, than to depend on the hurried work of two or three days.

The object which I had in view in writing this Address was to call attention to the fact that our present system

of training in chemistry does not appear to develop in the student the power of conducting original research, and at the same time to endeavour to suggest some means by which a more satisfactory state of things might be brought about. I have not been able, within the limits of this Address, to consider the conditions of study during the third year of the student's career at college, or to discuss the increasing necessity for extending that course, and insisting on the student carrying out an adequate original investigation before granting him a degree, but I hope on some future occasion to have the opportunity of returning to this very important part of the subject. If any of the suggestions I have made should prove to be of practical value, and should lead to the production of more original research by our students, I shall feel that a useful purpose has been served by bringing this matter before this Section. In concluding, I wish to thank Professor H. B. Dixon, Professor F. S. Kipping, and others, for many valuable suggestions, and my thanks are especially due to Dr. Bevan Lean for much information which he gave me in connection with that part of this Address which deals with the teaching of chemistry in schools.

SOME NEW SPECTRA OF RARE EARTHS.

By EUG. DEMARCAV.

TERBIA, one of the rare earths whose existence has been certain for a long time, owing to the existence of its coloured peroxide, is extremely ill-defined, because no spectra of terbia is known, nor even the true colour of the pure peroxide.

M. Lecoq de Boisbaudran showed that this substance, to which a pale colour had been attributed, was in reality very dark. However, even then it is not yet pure. I was able, indeed, to obtain from a specimen which was almost black, a spark spectrum in which several metals were present in apparently equal quantities. We can predict, however, without too great risk of error, that pure terbia peroxide will be as dark in colour as praseodymium peroxide, and that the simple yellow earths are contained only in very small quantities.

In the spectra of these various terbias I noticed several lines which seemed to belong to terbiu. They were strongly marked in the spectrum of M. Lecoq de Boisbaudran's brown terbia, together with lines belonging to various other elements. I obtained these terbia lines, together with the gadolinium lines, in the most soluble product of the magnesium nitrate of gadolinium which was already almost pure.

This very soluble product gives a brown oxide and a trace of the absorption band $\lambda=4877$, which M. Lecoq has attributed to Z_3 . I give the eight strongest lines belonging to this spectrum.

λ .	Intensity.	λ .	Intensity.
3704.3	10	3561.7	12
3703.2	11	3540.2	11
3676.7	12	3523.4	10
3568.4	10	3508.5	12

The maximum intensity being 16, minimum 1,

I provisionally have called the element having the above spectrum Γ . In the spectra of products rich in terbia, but approaching holmium, a second series of lines is apparent, brought out by certain fractionations in the less-coloured earth.

These correspond to a particular element in the neighbourhood of holmium, abundant in the dysprosium earths. Perhaps it is identical with Lecoq's earth Z_7 , identified by a band spectrum in the yellow portion of the spectrum. I shall call this element Δ , leaving the question as to its identity with Z_7 open.

The most prominent lines of this spectrum are:—

λ .	Intensity.	λ .	Intensity.
4212.6	11	3945.0	10
4195.5	6	3595.0	6
4187.3	9	3550.0	5
3978.6	6	3531.3	11

In the spectrum of the yttria earths, which are still more soluble and are intermediate between holmium and erbium, I notice two lines which are not due to either holmium or erbium. These two lines, which can be obtained very strong, have wave-lengths 3967.9 and 3930.9, and appear to belong to a particular element, which I will call Ω .

Finally, in the very slightly basic earths intermediate between erbium and ytterbium, several strong lines are seen, of which two (wave-lengths 4008.2 and 3906.5) do not seem to belong to thulium.

These strong lines may belong to $\Sigma-Z_4$. I am calling the elements to which these lines belong Θ .

I have also noticed, in addition to the various spectra mentioned above, a number of other lines due to elements already recognised by their absorption spectra. These spectra are not so marked as the others, having a much less bright spark.

As with the others, I have only obtained them as a mixture. The greater number of their lines and their faintness render the elements to which they belong still uncertain.—*Comptes Rendus*, cxxxi., No. 6.

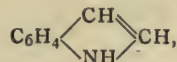
SYNTHETIC INDIGO.*

By EDWARD S. JOHNSON.

(Continued from p. 105).

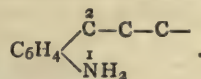
II. THE CONSTITUTION OF INDIGO.

THE leading motive of the classic investigations of Baeyer in the indigo series was the desire to establish "the place of each atom in the indigo molecule experimentally" (Baeyer, "Ueber d. Verb. Indigoreihe," *Ber. Deut. Chem. Gesell.*, xvi., 2188) and the relation of all bodies of the group to indol,—

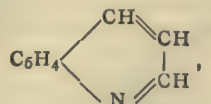


as generatrix (*Ber. Deut. Chem. Gesell.*, xv., 775).

It was by no mere chance that the formation of indigo from *o*-nitrocinnamic acid was discovered, but by a deliberately formed conclusion drawn from the facts observed in studying the linking of the nitrogen atom of an amido-group of a benzene ring, in ortho-position to a chain of two or more carbon atoms, thus—



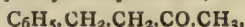
It was thereby and in the synthesis of bodies of the indigo group† found that the nitrogen of the amido-group unites with the second or third carbon atom of the chain, but not, it seems, with those more distant. The formation of such rings is not dependent upon the presence of the carboxyl-group. Thus a substance resembling quinoline,—



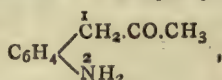
* *Proceedings of Engineers' Society of Western Pennsylvania*, xvi., No. 3.

† Throughout, the original discussion of the subject, as found in the literature to which reference has been or will be made, is here or will be in other similar instances closely followed.

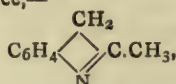
is formed when the third carbon atom is present in ketone-form as in phenylethylmethyl ketone,—



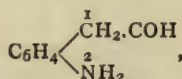
and it may be said in advance, with great probability of correctness, that whenever the second or third carbon atom is present as an alcohol, aldehyde, or ketone group, an inner anhydride will result, which belongs either to the indol or quinoline series. It was then further observed that the methylketone of *o*-amidophenylacetic acid,—



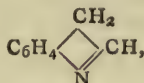
produces a substance,—



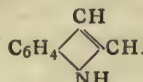
of the composition of a methylindol. If a ketone shows this reaction, it is to be expected that the corresponding aldehyde,—



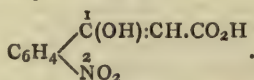
would give a body,



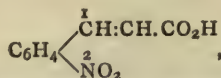
isomeric with indol,—



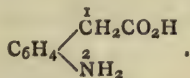
For this purpose, exactly as in the unnitrated body, it would be necessary to prepare the aldehyde by means of *o*-nitrophenyloxacrylic acid,—



This led then to the conviction that in *o*-nitrocinnamic acid,—



a better starting-point for the preparation of indigo, isatine, and indol would then be found in *o*-amidophenylacetic acid,—

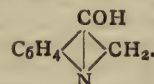


despite the loss suffered by the splitting off of carbonic anhydride (Bayer, "Ueber d. Bezieh. d. Zimmtsäure zu d. Indogruppe," *Ber. Deut. Chem. Gesell.*, xiii., 2254).

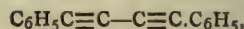
A series of most remarkable substances was developed—*o*-nitrophenylpropionic acid, isatogenic acid, indoxyl acid, indoxyl and derivatives, indoxanthinic acid, dinitrodiphenyldiacetylene, di-isatogen—and gave up under the persistent and skilful inquisition and acute perception of their discoverer the secret of the constitution of indigo.

The way through *o*-nitrophenylpropionic, isatogenic, and indoxyl acids to indoxyl gave important insight into the question. Indoxyl warmed with *o*-nitrophenylpropionic acid in alkaline solution yields indigo. Indoxyl, which is derived from *o*-nitrophenylpropionic acid, appears therefore possibly in the part of an intermediate product in the formation of the colouring matter which it produces when oxidised. Indigo, however, it was argued (Baeyer, I. "Ueber d. Verb. d. Indogruppe," *Ber. Deut. Chem.*

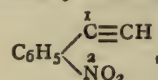
Gesell., xiv., 1741), is of much more complicated nature than indoxyl, giving, for instance, upon reduction substances of the character of complicated hydrocarbons. It is therefore more probable that, in the formation of indigo from indoxyl, a carbon condensation between two molecules of the latter takes place. The constitution of indoxyl, as then regarded by Baeyer, was represented by the following formula:—



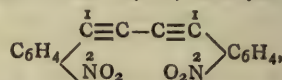
To obtain indigo, by condensation through the medium of oxidation, from indoxyl, the union must take place at the second carbon atom from the benzene ring, since the first carbon binds merely an hydroxyl-group. The hydrocarbon corresponding to such a union, Baeyer concluded, would be—



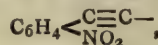
that is, Glaser's diacetylenylphenyl. To test this view, first the *o*-nitro-compound of the substance must be prepared. Direct nitration does not produce the desired result. *o*-Nitrophenylacetylene was therefore chosen as synthetic material. Numerous ineffectual attempts to unite two molecules of the monoacetylene compound,—



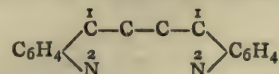
to one molecule of dinitrodiphenyldiacetylene,—



were made. This, notwithstanding, was finally accomplished by oxidation of the copper compound by alkaline solution of potassium ferricyanide. According to the mode of formation, it would be constituted as shown by the formula just given. The double occurrence in this combination of atoms of the group—

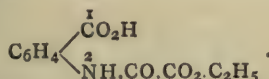


which makes its appearance in the formula of *o*-nitrophenylpropionic acid once, naturally suggested the probability of the formation of di-isatogen by the action of concentrated sulphuric acid in analogy with the formation of isatogen from *o*-nitrophenylpropionic acid under the influence of the same reagent. This actually proved to be the case. In the words of Baeyer:—"This substance claims great interest as being of all artificially prepared substances the one which stands nearest to indigo and is most readily converted into the colouring matter." Simply moistened with ammonium hydrosulphide, it is immediately transformed into indigo, and that quantitatively. The process is further a direct one, the substance instantly becoming blue upon contact with reducing agents without dissolving and without change of form. From the formation of indigo from *o*-nitrophenylacetylene, it appears, therefore, that the production from indoxyl is a double transformation consisting, first, in that the second carbon atoms (from the benzene ring) of two molecules undergo a condensation with the elimination of two atoms of hydrogen; and, in the second place, the body thus formed is converted into indigo by further oxidation. The existence in the indigo molecule of the atomic grouping—

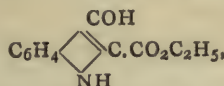


was thus experimentally established, wonderfully confirming Baeyer's deductions based upon the relation of indoxyl to indigo and the complicated structure of the latter. On account of the intrinsic interest of the subject

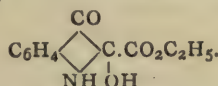
and intimate relation of the compound to indigo, it will be in place to consider further the observations which have led to a knowledge of the constitution of *isatogen* (Baeyer, II. "Ueber d. Verb. d. Indigogruppe," *Ber. Deut. Chem. Gesell.*, xv., 775). It was found that when isatogenic ethylester is reduced in aqueous solution with ferrous salts, that an ester, $C_{11}H_{11}NO_4$, is produced. This same substance is obtained by the gentle and cautious oxidation of indoxyl ethylester. The new substance, indoxanthinic ethylester, is converted by more vigorous oxidisers, such as chromic acid, into ethyloxalylanthranilic acid,—



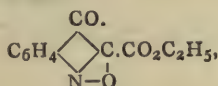
and is, moreover, readily re-converted by reduction into indoxyl ethylester, $C_{11}H_{11}NO_3$, which differ thus from indoxanthinic ethylester by one atom oxygen. The action of nitrous acid upon the latter produces a nitrosamine—an evidence of the presence in the molecule of the imido-group. Assuming for indoxyl ethylester the constitution—



and in view of its close relationship to this compound, the formation of a nitrosamine and the oxidation to ethyloxalylanthranilic acid, the formula of indoxanthinic ethylester would be—



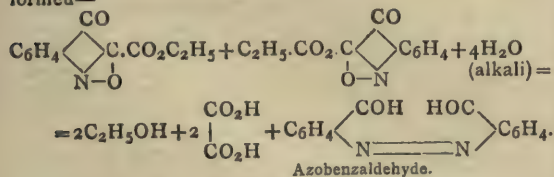
As already stated, the ester is derived by exceedingly cautious reduction of isatogenic ethylester. Representing this body by the formula—



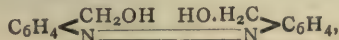
the transition to indoxanthinic ethylester is simply and perfectly explained: the bond between the oxygen and nitrogen atom is dissolved, and, by the addition of two atoms of hydrogen, the oxygen is changed to hydroxyl and the nitrogen to the imido-group as readily seen to be possible by a comparison of the formulæ. The characterising supposition is that of the existence of the atomic complex,—



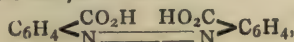
in the isatogen molecule. This is, further, in perfect accord with the fact that by the action of alkali *azo*-benzoic acid (the reactions are not given in detail in the original) is formed—



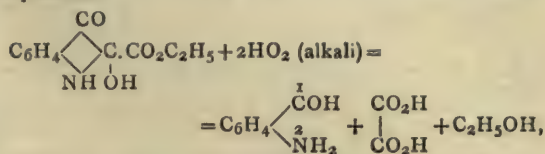
Under the influence of alkali, the aldehyde (two mols.) becomes, according to a general reaction, azobenzylalcohol,—



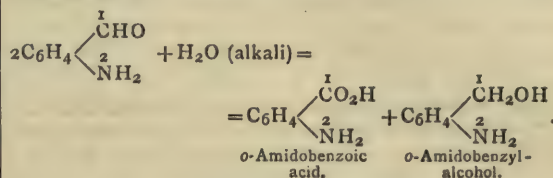
and azobenzoic acid,—



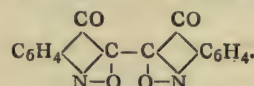
by the addition of two molecules of water. In a similar manner, from indoxanthinic ethylester, *amido*-benzoic acid is produced:—



with the intermediate formation thus of *o*-amidobenzaldehyde. This, as before, yields a corresponding acid and alcohol:—



To *di*-isatogen should therefore be ascribed the formula—



(To be continued).

ON TRI-IODIDE OF ARSENIC.

By R. DUPOUY.

TRI-IODIDE of arsenic is a therapeutic substance which was formerly very much used in the treatment of certain cutaneous affections. Of late years this medicament has been administered internally by Dr. R. Saint-Philippe, who has noted the good effects of iodide of arsenic on lymphatic and scrofulous children.

The medicament is supplied as a simple pharmaceutical preparation obtained by treating 1 grm. of iodide of arsenic with 100 grms. of water, and the liquid thus obtained goes under the name of "solution of iodide of arsenic." This name, however, is incorrect, for the water does not behave to the metalloidal iodide as a simple solvent, but, on the contrary, as a very energetic dissociating agent; and in reality it is not a solution of iodide of arsenic that is used in pharmacy, but rather a solution of arsenious anhydride and hydriodic acid, which are both products of the decomposing action of water on the tri-iodide of arsenic.

While studying the dissociation of iodide of arsenic by water, I have observed that most of the samples supplied commercially leave a residue of variable colour after treatment with water, and further, according to circumstances, the clear liquid obtained was sometimes odourless, but was, on the other hand, sometimes possessed of a very disagreeable smell. In face of such discordant results I thought it as well to make analyses of samples of iodide of arsenic, such as are actually sold, with a view to finding out the causes which make these samples behave in manners so different under the influence of the same chemical reagent, water.

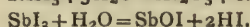
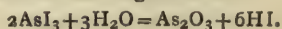
All the samples I was able to obtain belong to one of the four following types:—

Samples, I. The iodide of arsenic appears as a crystalline powder which, examined under the microscope, is seen to consist of hexagonal flakes.

Although this crystalline appearance tells in favour of the purity of the substance, chemical analysis shows that, on the contrary, this sample is not of absolute purity. When, in fact, we triturate 1 grm. of the iodide with 100

grms. of water, there remains a yellow residue which—when separated by filtration and dissolved in hydrochloric acid—gives a precipitate of sulphide of antimony with sulphuretted hydrogen; further, the presence of iodine in this yellow precipitate is easily shown; finally, when working on larger quantities and making a quantitative analysis, we find that the insoluble residue consists of the oxyiodide of antimony, SbOI .

The presence of this impurity is easy to explain when we remember that the arsenic used for the preparation of the tri-iodide sometimes contains antimony: it is evident, therefore, that if we act on this impure arsenic with iodine, there will be formed simultaneously iodide of arsenic and iodide of antimony, which occur, as is well known, under almost identical conditions. To purify the product we must have recourse to solution of the iodide of arsenic in sulphide of carbon; but it must be remarked that not only is iodide of antimony soluble in the same solvent, but, again, that it crystallises like iodide of arsenic in hexagonal flakes. It therefore follows that the crystalline powder contains both iodide of arsenic and iodide of antimony. If we act with water on this mixture we obtain the two following reactions:—



The second equation shows that oxyiodide of antimony is formed, and it is this body that forms the insoluble residue I have already referred to. We see that the water plays the part, to some extent, of a purifying agent, by removing from the iodide of arsenic the antimony it contains, by precipitating this latter body in the form of insoluble oxyiodide.

Finally, it must be remarked that iodide of arsenic, crystallised in sulphide of carbon, and then treated with water, gives a solution having a very disagreeable odour: this odour is that of the sulphide of carbon, which nearly always impregnates bodies crystallised in it.

Samples, II. The samples belonging to this second category occur in the form of masses or plates consisting of fused iodide of arsenic. When treated in the same manner as the last, we obtain a blackish precipitate after treatment with water, a part of which precipitate only is soluble in hydrochloric acid: this soluble part consists of oxyiodide of antimony. The black residue, insoluble in hydrochloric acid, when submitted to ordinary qualitative analysis, is found to be formed in greater part of metallic arsenic. These two impurities are a consequence of the method of preparation of melted iodide of arsenic. The oxyiodide of antimony takes its rise from an process analogous to that already described; as for the arsenic, its presence can be explained by the fact that, in reacting with iodine on arsenic, in the dry way, it is very difficult to limit the reaction of the two reacting bodies. One of them, the iodine, being more volatile, partly escapes the action of the arsenic which remains in excess, and which, being insoluble in water, remains as a residue after the treatment of the iodide of arsenic by this liquid.

Samples, III. These samples only differ from the preceding by the nature of the residue after treatment by water. The black insoluble precipitate is almost entirely formed of metallic arsenic; there are no traces of oxyiodide of antimony, which indicates that the arsenic which has been used for the preparation of the tri-iodide was free from antimony.

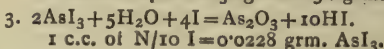
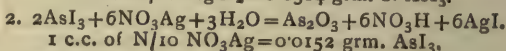
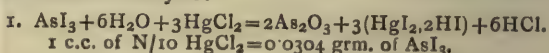
Samples, IV. The appearance of these samples examined is quite different to that of the others; of a deep brown colour, and having a very distinct odour of iodine, they stain the paper on which they may be placed, brown; these characteristics suffice to show the excess of iodine contained in these samples. Further, when treated with water they give a clear solution of a deep brown colour. This colouration sometimes disappears after a short while, for the excess of iodine probably reacts on the products of the dissociation of the iodide of arsenic, giving colourless products.

It results from the above analyses that the iodide of arsenic met with commercially is not chemically pure; it remains to be seen whether the amount of impurity is sufficient to prevent the therapeutic use of commercial iodide of arsenic.

If, for example, we weigh the residues obtained after treatment with water, from the first three groups of samples, we perceive that these precipitates, though very voluminous in appearance, are of very little weight, and the proportion of pure iodide of arsenic is not much diminished by the presence of the above-named impurities.

It is, at any rate, preferable to prepare a pure iodide of arsenic, or else to titrate that met with commercially. To effect this titration, it suffices to remark that iodide of arsenic can be estimated as a soluble iodide, either by Personne's method or by means of the more accurate cyano-argentimetric method described by M. Denigès ("Précis de Chimie Analytique"). Finally, iodide of arsenic can also be titrated as an arsenical compound of minimum oxidation by using iodine solutions, for example.

The three following equations sum up the above three methods, the details of which may be found in text-books of chemical analysis:—



In a future paper I propose to examine the methods of preparing chemically pure iodide of arsenic, and I shall lay stress upon the properties of this body, the chemical history of which is still very incomplete.—*Bull. des Trav. de la Société de Pharm. de Bordeaux*, June, 1900.

CORRESPONDENCE.

STANDARD OF ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—In accordance with your footnote (CHEM. NEWS, lxxxii., p. 66) I enclose my reply to Professor Volhard. I confess I was surprised to find such unanimity in the matter of a standard, for it usually takes a new suggestion many years to receive such general acceptance.—I am, &c.,

JAS. LEWIS HOWE.

Washington and Lee University, U.S.A.,
August 23, 1900.

Herr Prof. J. VOLHARD, Halle-a-S.

DEAR SIR—In reply to your questions in the CHEMICAL NEWS of August 10, regarding the standard of atomic weights, &c., I would beg leave to say:—

1. I prefer oxygen = 16 as the standard of atomic weights, for the reasons usually set forth in its favour. Using $\text{O} = 16$ as a standard of atomic weights, and not as a unit, I have not experienced the difficulties sometimes anticipated from a didactic standpoint.

2. I am of the opinion that as many figures should be given in expressing the atomic weights as are established with certainty, and one more which may be uncertain to the extent of several units.

3. I should be glad to have the International Atomic Weight Commission edit the current table of atomic weights on the above basis.

With highest esteem I have the honour to be yours very respectfully,

JAS. LEWIS HOWE.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Bradford Meeting of the British Association:—

President—W. H. Perkin, Jun., LL.D., Ph.D., F.R.S.
Vice-Presidents—Prof. H. E. Armstrong, F.R.S.; Horace T. Brown, F.R.S.; Prof. H. B. Dixon, F.R.S.; Dr. Gladstone, F.R.S.; W. H. Perkin, Sen., F.R.S.; Sir H. E. Roscoe, F.R.S.

Secretaries—W. M. Gardner; F. S. Kipping, Ph.D., D.Sc.; W. J. Pope; T. K. Rose, D.Sc. (*Recorder*).

Committee—A. H. Allen; Prof. Ossian Aschan; Sir William Roberts-Austen, K.C.B., F.R.S.; L. Blanc; C. H. Bothamley; J. B. Cohen, Ph.D.; T. Fairley, F.R.S.E.; Prof. W. N. Hartley, F.R.S.; A. Lapworth, D.Sc.; D. A. Louis; Prof. Stevenson Macadam, F.R.S.E.; F. H. Neville, F.R.S.; F. W. Richardson; S. Rideal, D.Sc.; Prof. A. Smithells; T. E. Thorpe, F.R.S.

The Papers brought before the Section were as follows:—

President's Address—The Modern System of Teaching Practical Inorganic Chemistry, and its Development.

Report of the Committee on the Teaching of Science in Elementary Schools.

Prof. E. A. Letts, D.Sc. and R. F. Blake—On some Problems connected with Atmospheric Carbonic Anhydride, and on a New and Accurate Method for Determining its Amount.

W. Ackroyd—On the Distribution of Chlorine in West Yorkshire.

W. Ackroyd—On a Limiting Standard of Acidity for Moorland Waters.

T. W. Hime, M.D.—On the Effects of Copper on the Human Body.

Report of the Committee on the Continuation of the Bibliography of Spectroscopy.

Report of the Committee on preparing a New Series of Wave-length Tables of the Spectra of the Elements.

H. B. Dixon, F.R.S., and F. W. Rixon, B.Sc.—On the Specific Heat of Gases at temperatures up to 400°.

Report of the Committee on the Nature of Alloys.

F. H. Neville, F.R.S.—Report on the Chemical Compounds contained in Alloys. To be followed by a discussion.

J. E. Stead—On the Mutual Relations of Iron, Phosphorus, and Carbon when together in Cast Iron and Steel.

J. A. Ewing, F.R.S., and W. Rosenhain, B.A.—On the Crystalline Structure of Metals.

Prof. Barrett, F.R.S.—On the Electric Conductivity of the Alloys of Iron.

C. S. Bradley—On some New Chemical Compounds Discovered by the Use of the Electric Furnace.

Report of the Committee on the Electrolytic Methods of Quantitative Analysis.

H. J. H. Fenton and Miss Gosling—Derivatives of Methylfurfural.

H. J. H. Fenton and H. O. Jones—A simple Method for comparing the Affinities of certain Acids.

W. J. Pope—Recent Developments in Stereochemistry. Followed by a discussion.

A. Lapworth—The Constitution of Camphor. Followed by a discussion.

Julius Bredt—On the Degradation of Camphor.

Prof. Ossian Aschan—On the Camphor Question.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on Isomorphous Derivatives of Benzene.

Report of the Committee on the Relation between the Absorption Spectra and Chemical Constitution of Organic Compounds.

W. R. Hodgkinson—Action of Aluminium Powder on some Phenols and Acids.

L. Limpach and W. R. Hodgkinson—The Direct Preparation of β -Naphthylamine.

C. F. Cross—Interaction of Furfural and Caro's Reagent.

S. Ruhemann and H. E. Stapleton—The Synthesis of Benzo- γ pyrone.

S. Ruhemann and H. E. Stapleton—Combination of Thiophenol and Guaiacol with Esters of Acids of the Acetylene Series.

H. D. Dakin and J. B. Cohen—Chlorination of Aromatic Hydrocarbons.

H. T. Brown, F.R.S.—On some recent work on the Diffusion of Gases and Liquids.

Dr. A. Liebmam—On recent Developments in the Textile Industries. Followed by a discussion.

H. M. Dawson, D.Sc.—On the Influence of Pressure on the Formation of Oceanic Salt Deposits.

Major-General Waterhouse—On the Sensitiveness of Silver to Light.

Dr. J. H. Gladstone, F.R.S., and G. Gladstone—Some Thoughts on Atomic Weights and the Periodic Law.

T. Fairley, F.R.S.E.—On the Relation between the Heating and Lighting Power of Coal Gas.

Dr. J. B. Cohen—On Smoke.

F. W. Richardson—On Bradford Sewage and its Treatment.

W. Leach—On the Treatment of Woolcombers' Effluents.

E. A. Letts, D.Sc., and R. F. Blake—On a New and Accurate Method for Determining Oxygen in Fresh Water, Sea Water, and Sewage Effluents.

W. B. Bottomley, M.A., Ph.D.—On the Utilisation of Sewage Sludge.

Messrs. John J. Griffin and Sons, Limited, have just issued their new Illustrated Catalogue and Price List of Bacteriological Apparatus, of 104 pages. It contains, besides the older and well-known apparatus specially designed for this branch of scientific work, all the latest improvements which have been introduced from time to time. There are also listed a number of pure living cultures and microscopical specimens of various bacteria, which will be found of great use by beginners as a help in the identification of microbes, as well as special sets of apparatus for tubercle and Gram staining, the detection of typhoid, &c. The catalogue concludes with two indices, one for names, the other for numbers.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Summer Term, 1900, there were fifty-two Students on the books. Of these, thirty-three were from Germany, five from Russia, four from England, two from Austria and two from France, one from Luxemburg, one from Sweden, one from Italy, one from Spain, one from the United States of America, and one from Rhodesia in South Africa. There were three Assistants in the Instruction-Laboratory, and twenty-four in the Versuchsstationen (private laboratories). In the certified body of Teachers there has been no change. To this body belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. Med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and T. Huber (Archited). The next Winter Term begins on October 15th. During the Summer Term, 1900, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of trade, manufacture, mining, agriculture, and hygiene.

The Decomposition of Silicates by Boric Anhydride.—P. Jannasch and H. Weber.—In the year 1895 Jannasch first proposed this method, which has since been shown to be insufficient for the attack of certain difficultly decomposable silicates, such as disthene and topaz. The authors have observed, however, that by sufficiently raising the temperature this process is capable of a general application. It is rapid, and allows of the estimation of all the elements of the mineral, including the alkalis, on a single sample. The finely powdered material is

mixed with 15 or 20 parts of powdered Bo_2O_3 . The whole is heated in a platinum crucible, first over a Bunsen burner, then over a blowpipe flame until in tranquil fusion. After partial cooling, 5 or 6 parts more of Bo_2O_3 are added, and the whole calcined over an oxyhydrogen blowpipe until the mass is completely transparent; this requires about a quarter of an hour. The gas from five to six ordinary taps must be brought to the blowpipe, and the oxygen injected by means of the second tube until the flame is no longer luminous. The contents of the crucible, which should remain limpid on cooling, are taken up immediately with a mixture of HCl and methylic alcohol, and heated gently on a water-bath until dry. This evaporation is repeated a second time with the same mixture; the expulsion of the Bo_2O_3 is very rapid. The analysis is then continued in the ordinary manner. It is as well to note that, in the case of fluoriferous silicates, the whole of the fluorine is given off in the state of BoF_3 , without any loss of silica, if we take care to use a sufficient excess of Bo_2O_3 . The method appears to be equally suitable in the case of fluosilicates and natural fluorides. —*Berichte*, vol. xxii., p. 1670.

The Ethylenediaminic Compounds of Palladium.—N. S. Koursanof and N. J. Gvosdaref.—The researches of Joergensen having shown that the compounds of ethylenediamine with the salts of platinum possess a high degree of stability, it appeared to be of interest to examine the analogous compounds of palladium, which, by the properties of its complex salts, forms the connecting link between the platinum metals and the Cu, Ni, Ag group. By the action of ethylenediamine on chloropalladate of potassium, K_2PdCl_4 , a rose-coloured precipitate is first formed, the composition of which is probably $\text{PdCl}_2 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{PdCl}_2$, and which re-dissolves in an excess of $\text{C}_2\text{H}_4(\text{NH}_2)_2$, giving a yellowish solution. On evaporation, this latter leaves colourless prismatic crystals of the composition $\text{PdCl}_2 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$. Contrary to what takes place with the corresponding platonic compound, this body is decomposed by dilute HCl; it loses 1 molecule of $\text{C}_2\text{H}_4(\text{NH}_2)_2$, and is transformed into $\text{PdCl}_2 \cdot \text{C}_2\text{H}_4(\text{NH}_2)_2$ in the form of small yellowish needles slightly soluble in water (1 part in 1000 parts of water at 17°). If we digest this new compound with an aqueous solution of thio-urea, $\text{C}_2\text{H}_4(\text{NH}_2)_2$ is again displaced, and we obtain red crystals of $\text{PdCl}_2 \cdot 4\text{CSN}_2\text{H}_4$, but we have not observed the formation of the complex body containing both $\text{C}_2\text{H}_4(\text{NH}_2)_2$ and CSN_2H_4 . Concentrated HCl easily dissolves $\text{PdCl}_2 \cdot \text{C}_2\text{H}_4(\text{NH}_2)_2$, giving a yellowish-brown liquid, which, on evaporation or cooling, deposits yellowish-brown plates, appearing violet by reflected light, which appear to result from the union of 2HCl with the preceding salt, and have the composition of the chloropalladate of ethylenediammonium, $\text{PdCl}_4(\text{C}_2\text{H}_4 \cdot \text{N}_2\text{H}_6)$, (type $\text{PdCl}_4\text{R}''$). This chloropalladate is soluble in water; the solution is of a yellowish-brown colour, but it gradually decomposes and deposits $\text{PdCl}_2 \cdot \text{C}_2\text{H}_4(\text{NH}_2)_2$. Heat accelerates this decomposition, the presence of HCl prevents it. The chloropalladate can be re-crystallised in concentrated HCl; we thus have an interesting case of mobile equilibrium dependent on the temperature and the concentration of the HCl:— $\text{PdCl}_2 \cdot \text{C}_2\text{H}_4(\text{NH}_2)_2 + 2\text{HCl} \rightleftharpoons \text{PdCl}_4(\text{C}_2\text{H}_4 \cdot \text{N}_2\text{H}_6) + 2\text{HCl}$. This decomposition is analogous to the reaction observed by Anderson with chloroplatinate of pyridine.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 691.

REDRUTH SCHOOL OF MINES, CORNWALL.

Principal—J. PAUL DE CASTRO, B.A. (Cantab.), A.I.C. F.C.S.

The Committee invite applications for the post of Demonstrator in the Chemical and Assaying Departments. The person appointed will have to give a short course of Lectures on the Elements of Metallurgy. Salary £80. Applications and testimonials should be received by the Principal not later than Sept. 18th. A copy of the Syllabus and further particulars will be supplied on application.

JAMES A. WINN, Registrar.

SOUTH-WESTERN POLYTECHNIC.

CHELSEA, S.W.

DAY TECHNICAL DEPARTMENT.

The usual College Courses in Civil, Electrical, and Mechanical Engineering and Applied Chemistry will be resumed on October 1st.

Fee for each Course, £15 per annum.

Particulars may be obtained from the SECRETARY.

BATTERSEA POLYTECHNIC, S.W.

DAY AND EVENING CLASSES IN INORGANIC, ORGANIC, AND TECHNOLOGICAL CHEMISTRY.

Head of the Chemical Department—Mr. JOHN WILSON, M.Sc.

Special Courses for London B.Sc. (Inter. and Final); Assaying and Technological Analysis (Gas, Water, Sugar, Oils and Fats).

Day Department for Applied Chemistry and Research Work.

For particulars apply to the SECRETARY.

BOROUGH POLYTECHNIC INSTITUTE,

103, BOROUGH ROAD

(Close to the Obelisk, Blackfriars Road, S.E.).

EVENING CLASSES (LECTURES AND PRACTICAL LABORATORY WORK), commencing MONDAY, SEPTEMBER 4th, 1900.

CHEMISTRY.—F. MOLLWO PERKIN, Ph.D., assisted by A. J. WALKER, Ph.D.

INORGANIC.—Elementary: Mondays and Wednesdays, 7.30—10. Advanced: Tuesdays and Fridays, 7.30—10. Fees 8s. to 10s. Special and Honours: Lectures, Tuesdays, 8.45—10; Laboratory Work—Mondays, Tuesdays, Wednesdays, and Fridays, 7.30—10. Fees, 8s. to 15s.

ORGANIC.—Elementary: Mondays and Wednesdays, 7.30 to 10. Advanced: Tuesdays and Fridays, 7.30—10. Fees, 8s. to 10s.

SATURDAY MORNING CLASS, 10—1. Fee, 10s.

ELECTRICITY & MAGNETISM.—JOHN

HENDERSON, D.Sc., A.I.E.E., assisted by H. S. SAUNDERS.

ELEMENTARY (Lectures and Laboratory).—Mondays, 7.30—10.

ADVANCED (Lectures and Laboratory).—Tuesdays, 7.30—10.

HONOURS (Lectures and Laboratory).—Fridays, 7—10.

Fees, 8s. and 10s.

The fees are Sessional, September to May, 1901.

Full particulars on application.

C. T. MILLIS, Principal,
Education Department.

ROYAL TECHNICAL INSTITUTE, SALFORD.

Principal W. WILSON, M.A.

The NEXT SESSION will Open on September 17th, 1900.

Full Day Courses and Evening Classes in various subjects, including CHEMISTRY and DYEING AND CALICO PRINTING.

Special Course for Print Buyers and Salesmen. Analysis of Dyes, Dye-ware, &c., and Gas Analysis.

Dyehouse contains Jigs and Plant for Experimental Dyeing of full width Calico, and in the Calico Printing Laboratory there is a complete range of full sized Machinery.

Prospectus and particulars free on application.

RICHARD MARTIN, Secretary.

NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 21st. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, Sept. 19th.

THE CHEMICAL NEWS.

VOL. LXXXII., No. 2130.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

WITH the advent of October the various Schools and Colleges for Scientific and Medical instruction again open their doors to students.

Every facility and encouragement is offered to those who care to take advantage of their opportunities. Many students are returning to familiar scenes and faces after a long vacation, in which they have been recuperating their energies and fitting themselves for further efforts in their advance towards the "degree" which will be, at any rate, the outward and visible result of their labours, if successful. Others, fresh from school, will find a great change in more ways than one. College life is much more free than the stricter routine of our school days; the Student is left more to the promptings of his own inclination, and is able to shirk many duties without apparently being any the worse off for it. It is to these younger students, commencing their careers, practically with the dawn of the twentieth century, that we would specially point out the urgent necessity of neglecting no opportunities; these, if not taken at the flood, may never recur again, and the words "too late" will be but a sad solace to a wasted youth.

As Sir Wm. Turner pointed out in his recent address to the British Association at Bradford, "diligence and accuracy" are fundamental qualities in scientific research; "by their application new facts are discovered and tabulated, but to decide on their true significance a well-balanced mind and the exercise of prolonged thought and reflection are needed." These latter qualifications will accrue later on in life, but "diligence and accuracy" should be the watchword of the student in these his college days.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin (two papers); English (two papers). Any one of the following Languages or Sciences:—Greek, French, German, Sanskrit, or Arabic; Mathematics (two papers); General Elementary Science (two papers); Elementary Mechanics, Chemistry, Sound, Heat and Light, Magnetism and Electricity, Botany.

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

The first six candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination will respectively receive an Exhibition or a Prize as follows:—The first of such candidates will receive an Exhibition of £30 per annum for the next two years. The second will receive an Exhibition of £20 per annum for the next two years. The third will receive an Exhibition of £15 per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific and Intermediate Examinations in Medicine, within three academical years from the time of his passing the Matriculation Examination. The fourth will receive a prize to the value of £10 in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of £5 in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a two days' practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year, — once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students

working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S. Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—J. Emerson Reynolda, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrators—W. Haughton, M.B., and W. C. Ramsden.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced, including Physical Chemistry, second year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Freshmen, and tenable for five years. These Foundation Scholarships are paid £20 per annum, have free commons, and their chambers and tutorial fees are at half the usual rates.

KING'S COLLEGE.

(DIVISION OF ENGINEERING, ARCHITECTURE, AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Demonstrator of Practical Chemistry—Herbert Jackson, F.C.S.

Assistant Demonstrator—P. H. Kirkaldy, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1900-1901 are October 4, January 17, and April 25.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visà voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of

Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor—William Ramsay, LL.D., F.R.S., &c.

Assistants—Morris Travers, D.Sc., Alexander Kellas, B.Sc., and E. C. C. Baly, F.I.C.

The Session is divided into three Terms, as follows:—First Term, from Tuesday, October 2nd, till Friday, December 21st; Second Term, from Tuesday, January 15th, till Friday, March 29th; Third Term, from Tuesday, April 23rd, till Friday, June 28th. Class Examinations begin on June 17th.

Junior Courses of Inorganic Chemistry.

First Term: Tuesday, Thursday, and Saturday at 10. Latter half of Second and Third Term: Tuesday, Thursday, and Saturday. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 15. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Mondays and Wednesdays, at 9, during the session.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1900-1901; also the Cloth-worker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D., B.Sc.

Assistants—G. S. Newth, G. T. Morgan, B.Sc., and J. A. Crow.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the

second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	£ 5	13
Physics	3	12
Biology with Botany	5	12
Geology with Mineralogy	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3

Mathematics and Mechanical Drawing, £3 per term. Model and Freehand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses. (See Science and Art Directory).

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-ninth Session will commence on Monday, October 1st, 1900.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S. (Dean); Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. UNIVERSITY OF WALES.

Professor—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Demonstrators—H. Hibbert, M.Sc. (Vic.), and A. Brooke. Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, October 2, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Course; four lectures weekly during the Lent and Easter Terms. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, two lectures weekly on Chemical Theory. (Courses A and B will generally be given in alternate Sessions; for 1900-1901, Course B). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Alexander Lauder, B.Sc., F.C.S. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton. Scholar Assistant, Alice E. Smith.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 2nd, 1900. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for

the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 8th, and terminates on June 28th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 50 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not in-

cluded in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Lecturer—Francis E. Francis, B.Sc., Ph.D.

Demonstrator—E. B. Ludlam, B.Sc.

The session 1900-1901 will begin on October 2. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the Session. Fee, £4 4s.

General Elementary Science (London Matriculation).—A course of about 16 Lectures will be delivered in the Third Term. Fee, including Physics (1st and 2nd Terms), £5 5s.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Junior and Senior Courses.

Advanced Course (Parts I. and II.).—One Lecture a week in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of

Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

General Elementary Science.—A course of Lectures, primarily intended for Candidates for Matriculation, will be given during the First Term. Fee (including Physics), 7s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY AND METALLURGY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell-Smith, B.Sc., A.I.C., F.C.S.; H. A. M. Borland, A.R.C.S.

Demonstrators—R. Tutton; F. B. Gatehouse; W. H. Collier (of the University of London)

Assistant in Chemical Laboratory—P. J. F. Pearson.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as

satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Evening Classes, available to persons of either sex, will commence on Monday, September 24th.

Further detailed information may be obtained from the College Prospectus, price 6d.

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., B.Sc., F.R.S.

Assistant Lecturer—C. F. Baker, Ph.D., B.Sc.

Demonstrator—W. R. Innes, Ph.D., M.Sc.

Lecturer on Metallurgy—Godfrey Melland, F.I.C.

The Session will be opened on October 2nd, 1900.

Lecture Courses.

A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Five hours weekly during the Winter and Spring terms. At least one of the above meetings of the class in each week will be devoted to tutorial work. Attendance at this tutorial class is compulsory, as is the performance of the weekly exercises set by the Professor. Mondays to Fridays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s.

B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Advanced Organic Chemistry.—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s.

General and Physical Chemistry.—This course will deal in outline with various Chemical subjects. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s.

A further Course on General and Physical Chemistry on special subjects attracting attention at the time. Fee, £1 11s. 6d.

Practical Chemistry.

This subject embraces three Courses. The Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is

given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD MUNICIPAL TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Head of Department—W. M. Gardner.

Lecturers in Chemistry—W. F. Sutherst, Ph.D. (Geneva), Chemiste-Diplômé de Zürich; and S. F. Sell.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Lecturer in Metallurgy—(Vacant).

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over three years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Chemical Philosophy, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over three years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Dyeing*. Extending over one or two years.

V. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VI. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading

groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer and Demonstrator—T. S. Patterson, Ph.D.

Demonstrators—J. McCrae, Ph.D., and H. M. Dawson, B.Sc.

The Session begins October, 1900.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.
2. Inorganic Chemistry.—Honours Course, Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.
3. Inorganic Chemistry.—Honours Course, Non-metals. Tuesday and Thursday at 9.30 a.m. Fee, £3 13s. 6d.
4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.
5. Organic Chemistry Honours Course.—Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.
6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.
7. Chemistry for Teachers.—Wednesdays from 2.30 to 5.30 in the first and second terms. Fee, £4 4s.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s. *Class in Practical Chemistry*, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S.E.

Assistant Lecturer—R. B. Brown.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Proßer, F.I.C.

Assistant Lecturer and Demonstrator—Andrew Turnbull, Ph.D.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to

sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—J. Seton, B.Sc.

Lecturer in Agricultural Chemistry—H. Ingle, F.I.C.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—C. A. Kohn, B.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers—T. L. Bailey, Ph.D., W. B. Davidson, M.A., D.Sc., Ph.D., C. A. Kohn, B.Sc., Ph.D., and A. W. Titherley, M.Sc., Ph.D.

Assistant—H. H. Froyssell.

The Session commences October 4th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry. Fee, £2.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Or-

ganic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work and research.

The William Gossage Laboratory, opened in 1897, consists of a large and well-fitted general Laboratory for advanced Students, a new gas analysis room, an additional lecture-room for Metallurgy and other classes, and an addition to the Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Four days	9	16 10s.
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course D or E, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D, E, and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the Victoria M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for on December 6, 7, and 8, 1900, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Principal not later than November 15.

Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—Saville Shaw, M.Sc., F.C.S.
Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—F. C. Garrett, M.Sc., F.C.S., and J. A. Smyth, B.Sc., Ph.D.

1. General Course.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Monday, October 8th. Fee, £3 10s. for the Session.

Second Year Course.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, extending from October to March, and a course of Lectures on Inorganic Chemistry from March to the end of the Session. The Class will meet on Tuesdays and Thursdays at 11 a.m., and Fridays at 3 p.m., and will commence on October 9th. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m.

Metallurgy and Assaying.—Lecturer, Saville Shaw, M.Sc., F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. **Laboratory Fees.**—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subject professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students

will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—

1. The first examination for the Degree of B.Litt.
2. Durham Examination for certificate of proficiency in General Education, held in March and September.
3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Tuesday, October 2nd.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers.—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; E. J. Russell, B.Sc.; D. L. Chapman, B.A.; and H. C. H. Carpenter, B.A.

Demonstrator in Organic Chemistry.—W. T. Lawrence, B.A., Ph.D.

Lecturer in Technical Organic Chemistry.—Jocelyn F. Thorpe, Ph.D.

Assistant Lecturer in Metallurgy.—Dr. Bone.

The Session begins on October 4, 1900.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Tuesdays, Thursdays, Saturdays, 11.30 a.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

METALLURGY.—*Lectures:* The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical:* The Metallurgical Laboratory will be open to students every day.

ELECTRO CHEMISTRY.—In connection with the new John Hopkinson Memorial Laboratory, rooms have been fitted for the study of Electricity in its applications to Chemistry. Courses of lectures and laboratory instruction will be given to Advanced Chemical Students in the coming Session. *Lecturer*—Mr. R. S. Hutton, B.Sc.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—
First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week).
Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week).
Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the College Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the Levinstein Exhibition; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate,

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—J. J. Sudborough, D.Sc., Ph.D., F.I.C., R. M. Caven, B.Sc., F.I.C., and G. D. Lander, D.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 8th. Evening Classes begin September 24th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbering, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Chemistry, Materia Medica, and other Pharmaceutical subjects.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tues-

day and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s. Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

Demonstrator—T. Slater Price, D.Sc.

The Session will commence on October 5th.

Beginners' Course.—Inorganic Chemistry: Tuesday from 10 to 11 a.m. Fee, £1 11s. 6d.

Matriculation Course.—Friday 10 to 11. Fee, £1 11s. 6d.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s.

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health and for the Licentiate of Sanitary Science, will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, M.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 10th, and ends on March 20th. The Summer Session extends from the middle of April to the end of June.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theo-

retical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, LL.D., F.R.S.

Demonstrators—W. B. Davidson, M.A., D.Sc., and W. Maitland, B.Sc.

I. *General Lecture Course* (100 Lectures).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £3 3s.; for subsequent attendance, £2 2s. A Tutorial Class (without fee), conducted by the Senior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry* (50 Lectures).—Daily during the Summer Session. Fee, £2 2s.

III. *Practical Course for Medical Students*.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis.

IV. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The fees depend upon the number of hours taken, and vary from £3 3s. to £6 6s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

In connection with the Laboratory work, two Lectures a week on Advanced Analysis and on Physical Chemistry are delivered (without extra fee) by the Senior Demonstrator.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

This course is given during the Winter Session, and includes both Lectures and Laboratory work. The Lectures deal with the chemistry of the atmosphere, the soil, manures, and foods. The physiological chemistry of plants and animals, the composition and manurial requirements of crops, and dairy chemistry, are also treated of. The Laboratory work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of soils, manures, feeding stuffs and waters, and with the impurities and adulterations of these, occupy much of the time given to practical work. The fee for the whole course—lectures and practical work—is £3 3s.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

Assistants—W. W. Taylor, M.A., B.Sc., J. P. Longstaff, and James Kerr, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.; and a class on Mineralogy and Crystallography, by Dr.

Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (i.e., Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy;

(2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—F. Grant Ogilvie, M.A., B.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assistant Professor—Allan W. C. Menzies, M.A., B.Sc.

Demonstrator—Andrew F. King.

The Session begins October 2nd, 1900.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

Chemistry.—The first course for day students is a combination of Lectures with Laboratory instruction. In the Lectures some of the more important elements and their compounds are discussed in detail, so as to lead to a knowledge of the general laws of chemical action. Other important elements are treated in less detail, and the relations and classification of the elements generally are broadly indicated. In the Laboratory each student will receive instruction in general chemical manipulation, in accurate weighing, volumetric measurements, and in some of the simpler methods of quantitative analysis. After making a series of simple preparations, he works through a number of experimental exercises illustrating chemical combination, oxidation, reduction, and double decomposition. These exercises are followed by instruction in simple methods of qualitative analysis, especial attention being given to dry way testing and the use of the spectroscope. Students attending a further course may take up the study of systematic analysis, and extend the knowledge they have gained of quantitative analysis by exercises in gravimetric, volumetric, and electrolytic methods. Ultimately they may make a speciality of any branch of the subject which may be most necessary for their future work. Great attention has been paid to the thorough equipment of Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Technical Chemistry—E. J. Mills, D.Sc., F.R.S.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1900-1901 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 10th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about forty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 28th and following days. Twenty-six of these Bursaries are restricted to Men and about fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. One Scholarship of £80, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1900-1901.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—

(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for

the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—Practical Chemistry.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—Laboratory Pupils.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four consecutive years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session begins on October 16th, 1900, and ends on June 8th, 1901. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) Two ordinary Courses of Practical Chemistry will be held, each of three months' duration; one commencing on January 4th, 1901, and adapted to the requirements of Students proceeding to the Examinations of the Royal University of Ireland; the other ending about the third week in June, and suitable for Medical Students intending to present themselves for the Examinations of other Licensing Bodies. Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students will be held in the second and third terms; fee, £5. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C.

Demonstrator—W. S. Mills, B.A.

The College Session, 1900-1901, commences October 16 and ends June 8.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commission for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship has just been awarded for the second time to a Chemistry Student of this College.

For Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN.

Professor of Chemistry—W. N. Hartley, F.R.S.

Assistant Chemist—J. Holms Pollak, B.Sc., Associate of the Royal College of Science, Dublin.

Demonstrator of Chemistry and Assaying—S. E. Bellanders.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Organic Chemistry; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £3 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

The following are supplementary courses of instruction:—

- (1) Laboratory Instruction in the Theory of Chemistry.
- (2) An Analytical Course for Students in Engineering.
- (3) A Course of Practical Chemistry for Medical Students.
- (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health.
- (5) Assaying.
- (6) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net.—*City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations began on Tuesday, September 18th, and the Winter Session opens on Tuesday, October 2nd. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers

and Teachers in special subjects. An examination for the admission of Students was held at the College on Tuesday, September 18th. Session begins October 2nd. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, F.C.S., &c. Session commences Oct. 1.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, M.Sc., and Mr. B. C. Polkinghorne, B.Sc. Day and Evening Classes in Science and Art subjects.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREAM'S BUILDINGS, CHANCERY LANE.—Chemistry Courses will be conducted, commencing September 26, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., B.Sc.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work (Session fees, per course, 8s. to 15s.), Dr. F. Mollwo Peikin, assisted by Dr. A. J. Walker. Physics: Evening Lectures and Laboratory Work (Session fees, per course, 8s. to 10s.), Dr. J. Henderson. Special Evening Courses on Oils and Fats, including Soap and Candle Manufacture, and on Painter's Oils, Colours, and Varnishes. Session opens Monday, September 24, 1900.

BRIXTON SCHOOL OF CHEMISTRY AND PHARMACY, 12, Knowle Road, Brixton, London.—Principal, Dr. A. B. Griffiths, F.R.S.E., F.C.S. Lectures on Chemistry, Physics, Botany, &c. The School is fitted with the best appliances, and there are collections of rare chemicals, metals, essential oils, &c. Medals and certificates are awarded to successful students. Practical Chemistry in all branches; and there are courses of Bacteriology, Biological Chemistry, and Research work for advanced pupils. The Laboratories are fitted with every convenience. For particulars apply, in writing, to Dr. Griffiths.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Herbert Tomlinson, B.A., F.R.S. Professor of Chemistry, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry, including Metallurgy, Oils and Colours, and Photography. Special Classes are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. Prospectuses of Day and Evening Classes may be obtained from the Secretary, 1d. each, by post 24d.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Mr. W. J. Pope; Assistants, Mr. S. J. Peachey and others. Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10.0, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties.

NORTHERN POLYTECHNIC INSTITUTE, Holloway, N.—Principal, J. T. Dunn, D.Sc. Evening Classes in Theoretical and Practical Chemistry. Assistants, Mr. H. Charles L. Bloxam and Mr. W. H. Watson, A.R.C.S. Prospectus containing detailed information of Chemistry Courses, as well as related Courses in Physics and other departments, may be obtained at the Institute.

NORTHAMPTON INSTITUTE (City Polytechnic), St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Lecturers in Technical Chemistry: Mr. C. J. Head, F.I.C., &c.; Mr. S. Field, A.R.C.S.; and Mr. J. E. Evans. Day and Evening Classes in Electro-chemistry. Electro-plating, Electro-metallurgy, Electrotyping and Stereotyping, and Gold and Silver Assaying. (For full details see Prospectus).

CARPENTERS' COMPANY TECHNICAL INSTITUTE, Jupp Road, Stratford, E.—Principal, William Ping, F.C.S. Session begins Sept. 24th. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School.

EAST LONDON TECHNICAL COLLEGE, People's Palace, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Demonstrator, F. G. Pope; Assistants, H. A. Phillips and A. J. Turner. Lectures and Practical Classes are held in the daytime in connection with the three years' course of the Day Technical College. Evening Classes are also held, offering instruction in the courses of the Science and Art Department and for the examinations of the University of London. The Day College opened on Sept. 10. Evening Classes begin Sept. 24.

S. THOMAS CHARTERHOUSE INSTITUTE AND SCHOOLS, Goswell Road, E.C.—President, Rev. Henry Swann, M.A.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

SOUTH LONDON SCHOOL OF PHARMACY, Lim., 325 and 409, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., and Mr. J. Thomas, B.Sc. (Lond.), Daily, at 12 noon. Lectures on Botany daily at 11 a.m. by Dr. Muter, and at 2.30 p.m. on Materia Medica and Pharmacy, by Mr. W. J. Mawer, Ph.C. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 5, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees: for the first term, 12 guineas; for the second and third terms, 10 guineas; and for the full session 27 guineas, inclusive of all departments. A special laboratory for training Advanced Students in Analytical Chemistry under the care of Mr. A. H. Mitchell Muter, F.I.C., F.C.S.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *via* the Institute of Chemistry Examination.

LONDON COLLEGE OF CHEMISTRY AND PHARMACY.—Principal, Henry Wootton, B.Sc.

METROPOLITAN COLLEGE OF PHARMACY, 100 and 162, Kennington Park Rd.—Principal, W. Watson Will, F.C.S.

THE CLIFTON LABORATORY, Berkeley Square, Bristol.—Principal, E. H. Cook, D.Sc. (Lond.), F.I.C. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Students are urged to undertake researches and receive special attention from the teachers. Every effort is made to produce thorough chemists rather than successful examinees.

LEEDS TECHNICAL SCHOOL (in connection with the Leeds Institute of Science, Art, and Literature), Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in 31 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc., A.R.C.S.; Mr. R. W. Ferguson, A.R.C.S.; and Mr. Chas. Walker, B.Sc.; Metallurgy, Theoretical and Practical, and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, and Practical Physics, by Mr. J. E. Tindall, B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker. Fees:—Lectures, from 2s. 6d. per Session;

Laboratory work, from 5s. Systematic courses arranged for Pharmaceutical Students and for those engaged in Chemical Industries at reduced composition fees. Session commenced Sept. 17th. Prospectuses of various Classes free on application to the Secretary, Mr. Arthur Tait. Calendar of the Institute (150 pp.) post free 4d.

LEEDS COLLEGE OF PHARMACY.—Principal, F. Pilkington Sargeant, F.C.S., &c.

THE MUNICIPAL TECHNICAL SCHOOL, Princess Street, Manchester.—At this important Municipal School, with an attendance of upwards of 4300 Students, there are organised Day Courses in Pure Chemistry, with applications to Dyeing, Bleaching, Printing, Brewing, and Metallurgy. In addition there are Evening Courses, not only in Pure Chemistry, but in Metallurgy, Mineralogy, Iron and Steel Manufacture, Brewing, Bleaching, Dyeing, and Printing, Coal Tar Products, Paper Manufacture, Gas Analysis and Gas Volumetric Calculations, Gas Manufacture, Technical and Commercial Analysis, the Chemistry of Oils and Fats, Chemical Engineering, Chemistry for Engineers and Builders, and Photography. The complete Syllabus (6d., by post 9d.) may be obtained on application to Mr. J. H. Reynolds, Director and Secretary, Princess Street, Manchester.

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, J. Paul de Castro, B.A. (Cantab.), A.I.C., F.C.S., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, and Blowpipe Analysis, for intending Assayers and Mineral Chemists. Shorter Courses are also held in the above subjects to meet the requirements of intending Mining Engineers, and Prospectors. Practical instruction in Mining given at Pednandrea, the School Mine. Syllabus on application to the Registrar.

READING COLLEGE.—Lecturer in Chemistry, C. M. Luxmoore, D.Sc., F.I.C. Assistants, J. L. E. Drugman, Ph.D., and W. J. Monk. Autumn term begins Oct. 3.

TECHNICAL INSTITUTE, SALFORD.—Principal, W. Wilson, M.A. Session begins September 12th. Special attention is directed to the Dyeing and Calico Printing Laboratories. Day and Evening Classes in Science subjects. Also School of Art. Particulars free from Secretary.

STOCKPORT TECHNICAL SCHOOL.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application. Special instruction is given in the Dyeing of Felt, &c., as applied to Hat Manufacture.

WOLVERHAMPTON FREE LIBRARY SCIENCE AND TECHNICAL SCHOOL.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Mr. H. J. Tench; Botany, Mr. Sidney Phillips, Ph.C.; Latin, Mr. F. G. Griffiths, M.P.S. Day Classes in Chemistry and Physics, and Evening Classes in Chemistry, Physics, Botany, French, Latin, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. The School is recognised by the Examining Board of the Royal College of Surgeons and Physicians, as a centre for preparation in Chemistry and Physics. Session commenced Monday, Sept. 17th. For other particulars and programme, apply Mr. J. Elliot, Secretary.

Analyst requires temporary use of Chemical Laboratory in London for Mineral Analyses, &c.—State weekly rental, including use of necessary Apparatus and Chemicals, &c., to "Zero," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Advertiser requires position as Chemist or Assistant Manager in Works. Six years' experience in Works in England, including entire control, and two years Assayer in mines abroad. Honours Science Graduate, M.Inst.M.E.—Address, E. E., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London.

Situation as Chemist or Assayer required by young man, A.I.C. Three years at College; three years in Public Analyst's Laboratory; and one and a-half years in Works as Assayer. Good references.—Address, A.19, CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

THE CHEMICAL NEWS.

VOL. LXXXII., No. 2131.

ON SOME PROBLEMS CONNECTED WITH ATMOSPHERIC CARBONIC ANHYDRIDE, AND ON A NEW AND ACCURATE METHOD FOR DETERMINING ITS AMOUNT, SUITABLE FOR SCIENTIFIC EXPEDITIONS.*

By Professor LETTS, D.Sc., Ph.D., &c., and R. F. BLAKE,
F.I.C., F.C.S., Queen's College, Belfast.

ATTENTION is drawn to the variations in the amount of atmospheric carbonic anhydride which correspond with at least 10 per cent of the total amount, the causes of which are still to a large extent obscure. In the authors' opinion the subject is an important one, and is worthy of a systematic investigation by a number of skilled observers working in different localities and employing the same method of determination which shall have been proved to give results which do not vary from the true amount by more than three or four parts per million of air. Among the problems relating to atmospheric carbonic anhydride which the authors think are specially deserving of attention are the following:—

1. *Is Schläesing's Theory Correct?*—Do the oceans really act as regulators of the amount of atmospheric carbonic anhydride by the production or dissociation of earthy bicarbonates according as the amount rises above the normal or falls below it? As consequences of this theory latitude should influence the quantity of atmospheric carbonic anhydride, which ought to be lower in polar than in tropical localities, and the great ocean currents should also have an effect as they pass from warmer to colder regions, or the opposite.

2. *The Influence of Day and Night at Sea.*—To account for the increased quantity of atmospheric carbonic anhydride over land surfaces at night, which most of the observers have found, two theories have been advanced: (a) cessation of plant activity in decomposing the gas owing to the absence of light, and (b) the streaming out of ground air from the soil owing to the lowering of temperature.

At sea no such influences can be exerted, but an absorption of atmospheric carbonic anhydride may occur at the surface of the water owing to lowering of temperature, thus reversing the land effect.

3. *The Effects of Atmospheric Precipitates, and especially of Snowfall, which appears to increase the amount of Atmospheric Carbonic Anhydride.*—No reasonable theory has been advanced to account for this curious phenomenon, and it would be interesting to ascertain whether it occurs at sea as well as on land; and the same remark would apply to fog and rain, both of which appear to affect the amount also.

Other supposed causes of variation are worth studying, such as the effects of the seasons, direction and force of the winds, the prevailing type of weather, &c. But those which the authors think most interesting are such as a scientific mission would be under peculiarly favourable conditions for observing, and especially the proposed Antarctic expeditions.

In a memoir of the authors recently published in the *Proceedings of the Royal Dublin Society* (vol. ix., N. S., Part II., No. 15) a modification of Pettenkofer's process

for determining atmospheric carbonic anhydride is described by means of which results of great accuracy may be obtained. Thus, in the final set of test experiments with artificial mixtures of purified air and carbonic anhydride in known volumes, a mean error (in six determinations) of about 1 per cent of the gas was found, corresponding with some four parts per million of air taken.

For use by a scientific expedition it seemed, however, to the authors that a different process is required, in which the operations at the place of observation should be as simple as possible, and of such a nature as to permit of the actual determinations being made at any convenient time later, when the resources of a properly equipped laboratory are available.

The authors have accordingly devised a method which fulfils these conditions, and which is simple and accurate. On the one hand, it resembles Pettenkofer's process in that a relatively small volume of air is examined (about 6 litres), while, on the other, Müntz and Aubin's principle is adopted of absorbing the carbonic anhydride by caustic potash solution and afterwards liberating it by ebullition *in vacuo* with an acid, and measuring its volume in a suitable gas analysis apparatus.

A series of sealed tubes is prepared in the laboratory, each tube containing an accurately measured volume of weak potash solution (the amount of combined carbonic anhydride which such a solution always contains having been ascertained for a given stock).

The only operations which have to be performed at the place of observation are the collection of the air sample in a suitable receiver; the transfer of the contents of one of the sealed tubes to the latter, and, after absorption of the atmospheric carbonic anhydride, their re-transfer, as far as possible, to the same tube, which will be again sealed. The tubes can, of course, be kept for an indefinite period both before and after their contents have been thus treated, and the determination of the absorbed carbonic anhydride made, when convenient, with an aliquot portion of their contents. The experiments made to test the accuracy of the new method were satisfactory. Artificial mixtures of purified air and carbonic anhydride in definite volumes were employed (the two being in about the proportion they occur in ordinary air). Five determinations in such mixtures gave a mean error of 1·3 per cent of the carbonic anhydride taken, equivalent to 4 parts per million of air.

NEW SILICON COMPOUNDS OBTAINED BY THE USE OF THE ELECTRIC FURNACE.*

By CHARLES S. BRADLEY.

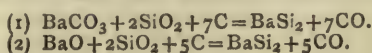
THE compounds in question are silicides of calcium, barium, or strontium, from which, by a secondary step, silico-acetylene is obtained.

They have the formula CaSi_2 , BaSi_2 , and SrSi_2 respectively, and are the silicon analogues of the alkaline earth carbides, while the silico-acetylene is the analogue of acetylene having the formula Si_2H_2 when the carbonates or oxides of the alkaline earths are mixed with silica in the form of ground quartz or sand, in which the relative atomic proportions of the alkaline earth metal to the silicon in the mixture is as 1 to 2, and sufficient carbon to effect the reduction is added, or when silicates of the alkaline earth metals in which the atomic relation of the earth metal to the silicon is as 1 to 2, are mixed with sufficient carbon to take up the oxygen of the compounds present, and heated in the electric furnace under conditions substantially like those maintained in the manufacture of alkaline earth carbides, silicides of the alkaline earth metals are produced.

* Read before the British Association (Section B), Bradford Meeting, 1900.

* Read before the Chemical Section of the British Association, Bradford Meeting, 1900.

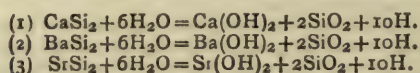
As an example of the process the following reactions for the formation of barium silicide from the barium compounds may be given:—



Calcium and strontium silicides are formed by exactly similar reactions from similar compounds. They are white or bluish-white substances of metallic appearance, and also resemble aluminum silicide and silicon somewhat in appearance.

They possess a distinctly crystalline fracture, showing plate-like crystals very similar to those seen in the fracture of cast zinc, the crystals being, however, somewhat smaller in size.

They oxidise slowly in the air and more rapidly under the influence of heat, yielding silicon dioxide and the oxide of the alkaline earth metals present. Like the carbides they are decomposed by water, but yield, instead of acetylene, hydrogen in a pure state, which is evolved without explosion, the following being the reaction:—



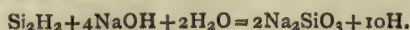
The calcium compound dissolves slowly in cold water but more rapidly in hot water; the barium compound decomposes rapidly in both cold and hot water. The strontium compound dissolves more rapidly in water than the calcium, but not so rapidly as the barium compound.

It will be noticed, by considering the equations 1, 2, and 3, that all of these compounds evolve large volumes of hydrogen:—

- 1 lb. CaSi_2 producing 0.104 lb. or 18.73 cu. ft. hydrogen at 0°C . and 760 m.m.
- 1 lb. BaSi_2 producing 0.051 lb. or 9.15 cu. ft. hydrogen at 0°C . and 760 m.m.
- 1 lb. SrSi_2 producing 0.069 lb. or 12.36 cu. ft. hydrogen at 0°C . and 760 m.m.

Calcium silicide, when treated with dilute acids, either the oxy-acids or the hydrogen acids, gives rise to the formation of a new compound which has the formula Si_2H_2 , and is therefore the silicon analogue of acetylene, C_2H_2 , and must be called silico-acetylene, since it bears the same relation to silico-methane (silicon hydride), SiH_4 , as acetylene bears to methane, CH_4 , the reaction being $\text{CaSi}_2 + 2\text{HCl} = \text{CaCl}_2 + \text{Si}_2\text{H}_2$. Silico-acetylene is a yellow crystalline compound, and differs in properties from the compound SiH_3 which Ogier obtained by sparking SiH_4 , which was unstable and exploded when subjected to a shock, Si_2H_2 being stable or non-explosive at ordinary temperatures.

When treated with 20 per cent solution of caustic soda or potash, (Si_2H_2) yields hydrogen according to the following equation:—



Heated in air this compound, Si_2H_2 , oxidises rapidly, giving $2\text{SiO}_2\text{H}_2\text{O}$, and when heated in a closed tube it breaks down into amorphous silicon and free hydrogen. Strontium silicide, when treated with a strong acid, does not produce silico-acetylene with the same facility, while the barium compound when so treated produces a mixture of gaseous compounds and free hydrogen. These silicides can be produced at low cost where electric power is cheap, are very powerful reducing agents, and it is hoped will find large use in the dye industries. Some experiments have been tried on molten steel carrying phosphorus and sulphur, and the requisite quantity of silicide of barium or calcium completely removed these impurities as well as all oxygen present. These compounds were discovered and examined by Mr. Charles B. Jacobs, of New York,

ELECTROLYTIC COPPER REFINING WORKS.

A LARGE field of applied electrical engineering has been developed of late years in connection with mining work. Not only has electricity been brought to the aid of the miner, working underground, but, after the raw materials are brought to the surface, in the various processes of the purification of the metal, it holds sway. As a means of producing motive power, electricity holds its own against its rivals—steam, gas, water-power, &c.—chiefly by virtue of its economy, adaptability, and flexibility; as a means of producing chemical effects, electricity stands unrivalled, and for this reason one of the most important of modern industries is that of applied electro-chemistry. The equivalent of thousands of horse-powers of electrical plant are already in use for the separation and purification of various metals.

The Boston and Montana Copper and Silver Mining Company of Great Falls, Montana, have one of the largest and best equipped copper refining works in the world. The power required for these works is obtained from the river, the power-house being placed on the bank about 3 miles above the town of Great Falls. Here is installed a twin water-wheel, working under a head of 50 feet of water. This wheel develops 2000 h. p. at 130 revolutions per minute, and drives two large electrical generators.

The generators, which are direct coupled, one at each end of the water-wheel shaft, are of Westinghouse construction, and are each capable of yielding continuously 1220 k. w. at 220 volts pressure. They run on this full load continuously, seven days a week, day and night. The field magnets of the machines are divided vertically, and each half slides on horizontal guides, thus leaving the armature accessible without the necessity of disturbing any of the machine bearings. This arrangement is very convenient where head-room is limited and cranes are not at hand for lifting heavy weights. The coupling between the water-wheel and each generator consists of two steel discs, each with projecting studs or pins. A strong leather ring is placed over each corresponding pair of studs, one on each disc. The brush-holders are carried on a ring supported on the field magnets; by this arrangement the commutator of the machine is left as clean as possible for cleaning and inspection.

The lead of all the brushes is adjusted simultaneously by a hand-wheel on a worm shaft gearing on to the rim of the supporting ring.

The generators are independently excited by means of two small Westinghouse generators yielding current at a 125 volts pressure.

The switchboard for the control of this plant is 7 feet 6 inches in height and 10 feet long. It is split up into panels, four carrying the regulating gear of the main generators, and one the regulating gear for the exciters. The whole is of Westinghouse construction; the four large single-pole switches for the main generator circuits have a carrying capacity of 6000 amperes each.

The works containing the copper refining plant is situated on the summit of a hill about half a mile away from the power-station. There were two courses to choose from as to how the electrical energy should be conveyed from the generating works to the refining plant. It meant either raising the pressure of the current to a high value and installing a light transmission line, in which case large converting plant would have been necessary at each end; or it meant keeping the initial low pressure, installing a conductor of large cross-section between the two places, and not requiring any converter plant whatever. The latter arrangement was adopted, and the mains between the power-house and the refining works are exceptionally large. They are of copper strip or plate, 12 inches wide and 2 inches thick, supported the whole way on wooden scaffolding at a height of about 12 feet above the ground.

The copper ore, as it comes from the earth, is ground up and concentrated. The rough metal is then melted

up, cast into pigs, and sent on the works we are dealing with—the refining works.

The refining process is carried out in a number of electrolytic baths. The pigs of metal are each about 2 feet square and 2 inches thick, with a pair of projecting lugs at one end. They are hung on the baths by these lugs from conducting brackets. Thin copper sheets are hung between the pigs and from the cathodes of the bath. The pigs are thus split up, and the refined copper is deposited on the thin sheets. The refuse from the copper pigs falls to the bottom of the bath. It consists chiefly of lead, silver, and gold, and is stated to be worth about £520 a ton; the value of the quantities of gold, silver, and lead extracted from these residues being sufficient to pay for the whole electrolytic process. Work in this refining process is carried on quite continuously, and thus the electrical plant is put severely to the test, and is found to acquit itself perfectly.

The works of the Anaconda Copper Mining Company have also been equipped with electrical plant. Here are installed nine Westinghouse electrolytic generators. Three of these are driven by belt from steam-engines, run at 260 revolutions per minute, and are each capable of producing 3600 ampères at 75 volts pressure. Four other similar-sized machines are direct coupled to steam-engines, and the remaining two are larger-sized generators, 4800 ampères at 75 volts, also direct coupled to steam-engines. A peculiar feature of these electrical generators is that each of them is provided with two commutators, one at each end of the armature, the object being to collect the large currents without undue heating at the points of commutation. In addition to the prevention of commutator heating, the weight is more evenly distributed on the machine bearings, and better brush contacts are secured. The rest of the construction of these machines is practically similar to those supplied to the Boston and Montana Company.

These works are lighted by electricity generated by a Westinghouse alternator driven by water-wheels.

The published annual report of the Boston and Montana Company for 1898 tends to show that the business of copper refining is a profitable one. Their sales of copper, gold, and silver amounted to about £1,500,000, and after payment of all expenses the amount applicable to dividends was £700,000.

It is therefore little to be wondered at that many new works are being opened in the various parts of the United States for the development of this business.

THE UNIVERSAL EUDIOMETER.

By G. H. WOOLLATT.

This instrument is designed to give accurate readings of the temperature, pressure, and volume of a gas through a considerable range of all or any of these factors. It is therefore specially suitable for the demonstration of the laws of Boyle and Charles, and for the analysis or synthesis of gases.

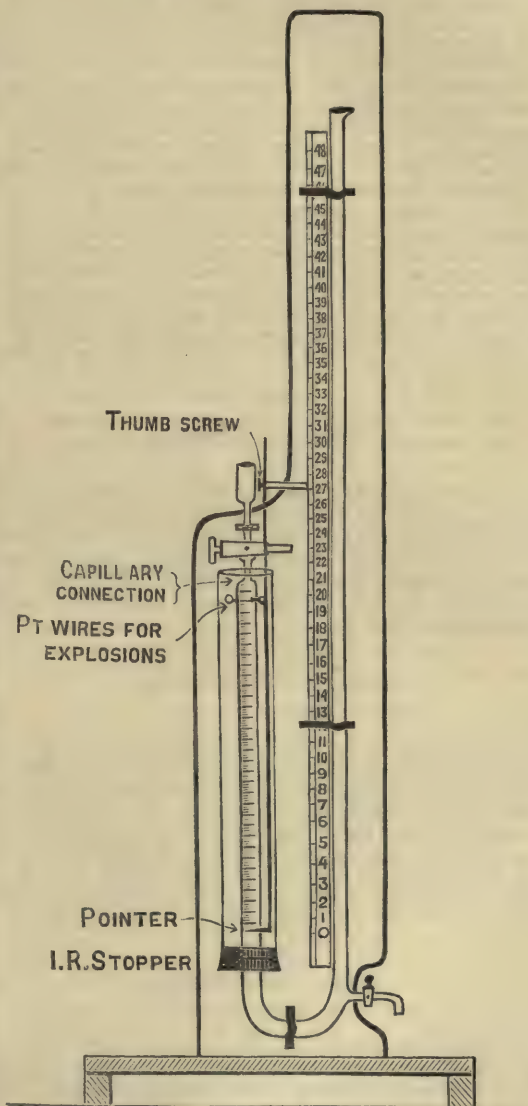
It consists essentially of a U-tube, one limb being jacketed and closed at the top by a three-way cock, the other extending open to a height somewhat over 1 metre. The short limb is provided with explosion terminals, is accurately graduated in volumes, and the shape is such as to allow the whole contents of the tube to assume the temperature of the liquid in the jacket, while still giving easy access to the three-way cock. In order to use a minimum amount of mercury, the longer limb is made of smaller diameter than the short one.

A movable scale, graduated in tenths of inches or centimetres, slides up and down by the side of the longer limb outside the jacket, and a pointer rod attached to the scale slides inside the jacket close to the graduations, the pointer corresponding exactly to the zero of the scale.

In measuring volumes and temperatures, the readings are taken as usual.

(a). *For Pressures Exceeding Atmospheric.*—The pointer is brought to the mercury level in the eudiometer tube, and the height at which the mercury stands—as shown on the scale—in the longer limb, is added to barometric pressure.

(b). *Less than Atmospheric.*—The pointer rod is raised by means of a thumb screw until it corresponds with 10,



20, 30, or 40 c.m. (as is most convenient) on the scale. This is shown by lines engraved on the pointer rod. The pointer is brought to the mercury level in the eudiometer tube as before, and the difference of levels (as read from the scale) subtracted from barometric pressure.

The accompanying sketch will show the type of apparatus. It has proved of the greatest help in lecture demonstrations, giving accurate results with very little trouble, and over a wide range of conditions.

SYNTHETIC INDIGO.*

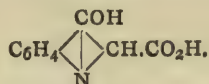
By EDWARD S. JOHNSON.

(Concluded from p. 129).

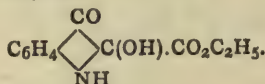
II. THE CONSTITUTION OF INDIGO (*continued*).

Of the remaining atoms of the indigo molecule, two each of hydrogen and oxygen, and the question as to the former's combination with nitrogen, still require consideration and disposition. They have been fixed in their relationships to the others by researches which discovered the constitution of indoxyl acid and its derivatives. Of the latter, the oximes or isonitroso-compounds, and of isatine as well, are of first importance. The study of the reactions of indoxyl with the aldehydes and ketone acids, with isatine and ethylpseudoisatine threw additional light upon the subject, and incidentally discovered the chromophoric group of indigo; they furthermore strongly corroborated the evidence adduced by the investigation of the nitrous acid derivatives of indoxyl and isatine.

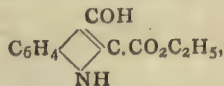
If in indoxyl acid (ester), which is transformed by gentle oxidation into indigo, the position of the oxygen be established and the question as to the existence of the imido-group in its molecule be answered, the positions of the extra-benzene hydrogens and the two oxygen atoms in indigo are likewise as definitely determined. The constitution of indoxyl acid (ester) as assumed by Baeyer immediately after his earlier investigation of the subject was—



It will be recalled that the acid was formed from indoxyl ethylester, which in turn was obtained by reduction of isatogenic ethylester. As already pointed out in another connection, indoxyl ethylester becomes by gentle oxidation indoxanthinic ethylester. In consideration of all pertinent circumstances, the formula of this substance can only be—

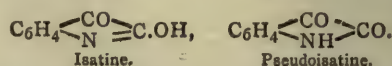
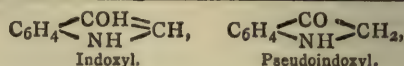


The presence of the imido-group, which is an essential feature, is demonstrated by the formation of a *nitrosamine*. Reduction of indoxanthinic ester forms indoxyl ester in which the presence of the imido-group must likewise be assumed, it being highly improbable that in the reduction the imido-hydrogen of the indoxanthinic ester should be removed (Baeyer, II., "Ueber d. Verb. d. Indigogruppe, V.," *Ber. Deut. Chem. Gesell.*, xv., 775). The formula of indoxyl ester should therefore be—

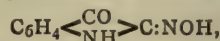


and not as first published. The presence of the imido-groups and a corresponding position of the oxygen atoms in indigo may be presumed with a like degree of certainty.

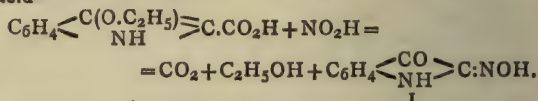
In his extended research upon the nitrous acid derivatives of indoxyl and isatine, Baeyer found that these bodies react according to two formulæ, those representing them in the free state, and other isomeric combinations designated pseudo-forms and corresponding to certain derivatives conceived as generated from the first by the migration of an hydrogen atom. The pseudoforms exist only as derivatives. The formulæ below will explain the distinction:—



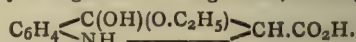
Among the derivatives of these combinations, *isonitroso-pseudoindoxyl* or *pseudoisatine-α-oxime*,—



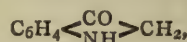
is of great interest from its still more direct bearing upon the question of the position of the oxygen atoms and the existence of the imido-groups. The compound is produced by the action of nitrous acid upon ethylindoxyl acid—



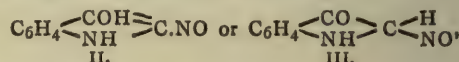
Water may be regarded as being added, forming—



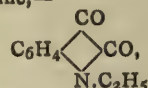
The splitting off of alcohol and carbonic anhydride would leave—



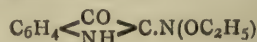
which with nitrous acid gives the isonitroso-compound. That a body of the given composition (I.) and not of two other possible configurations results,—



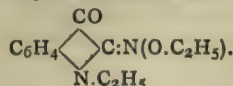
was demonstrated by the behaviour of the ethylation product obtained by the use of one molecule of ethyliodide and sodium alcoholate. In the first place, the derivative by reduction and subsequent oxidation yields isatine, and not ethyl(pseudo)isatine,—



showing thus the ethyl-group not to have substituted hydrogen in the imido-group, but, if Formula I. be correct, in the hydroxyl of the isonitroso-group. Formula II. would require substitution in the hydroxyl and a compound unstable to boiling acid; the substance, on the contrary, resists decomposition by boiling concentrated hydrochloric acid. If III. be assumed, the ethylation must have taken place on the carbon atom binding the nitroso-group—a supposition inconsistent with the easy transformation, by the successive processes of reduction and oxidation, into isatine. Of the three discussed expressions for the substance,—



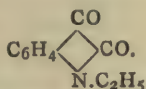
is most in accord with its behaviour. By further action of the sodium alcoholate and ethyl iodide (one mol. each), one (Baeyer, IV., "Ueber d. Verbindungen d. Indigogruppe, V.," *Ber. Deut. Chem. Gesell.*, xvi., 2188) more ethyl-group was introduced. The resulting compound, its mode of formation, its analysis, its resistance to alkalis and even boiling acids considered, must be constituted as indicated by the formula below:—



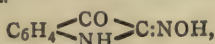
This compound, *ethylpseudoisatine-α-ethyloxime*, was converted by Baeyer by very gentle reduction into *diethyl-*

* *Proceedings of Engineers' Society of Western Pennsylvania*, xvi., No. 3.

indigo. Oxidation of this compound produces ethylpseudoisatine,—

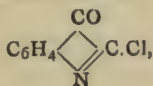


This reaction together with the process of formation furnishes indubitable evidence that the ethyl-groups of diethylindigo are bound by nitrogen. Confirmative of these observations and in analogy with the first, *pseudoisatine- α -oxime*,—

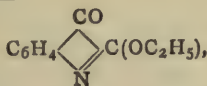


by the same agency produces *indigo*. By these remarkable experiments, the existence of the imido-groups in the indigo molecule was established, and the position of the oxygen atoms given beyond reasonable doubt.

As confirming the conclusion with reference to the disposition of the oxygen atoms, Baeyer directs attention to the fact that the moderate reduction of isatine chloride,—

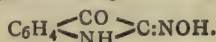


and ethylisatine,—

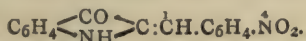


both bodies of the indigo group, which contain oxygen combined with the carbon atom next to the benzene-ring, and only such, produce indigo.

From still another standpoint, the question as to the constitution of indigo has been illuminated. Baeyer observed that mixtures of aqueous solutions of *indoxyl* with certain aldehydes give rise to stable red precipitates, accompanied by the formation of one molecule of water. *p*-Nitrobenzaldehyde, to take a simple instance, undergoes a similar reaction. Indoxyl and nitrous acid likewise produce a yellowish red precipitate, also with the separation of one molecule of water. These phenomena, it was concluded, were of themselves sufficient evidence for the assumption of similarity of constitution. The conclusion, however, became unquestionable when it was discovered that both (the nitrous acid derivative after substitution of the hydrogen of the oxime-group by ethyl) form with sodium alcoholate blue salts whose solutions in chloroform show the spectrum of *indigo*. The nitrous acid derivative is the already discussed pseudoisatine- α -oxime,—



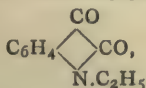
By analogy, the compound from *p*-nitrobenzaldehyde would be—



Such bodies Baeyer denominated *indogenides*, and the dyad atomic complex—

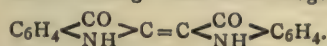


contained by them all, *indogen*. Its substitution in place of oxygen in the simple aldehydes (acetaldehyde, benzaldehyde), and others by application in aqueous solution, produces *yellow* crystalline unstable substances. When derived from other more complicated aldehydes (*p*-nitrobenzaldehyde, terephthalic aldehyde), and also benzaldehyde (with indoxyl in dry condition), *red* stable precipitates are obtained. With *ethylpseudoisatine*,—



an indogenide remarkably resembling indigo in properties

is formed. Finally, the synthesis of indigo from pseudoisatine- α -oxime, whose constitution has had detailed consideration, discovers indigo itself as *di-indogen*,—



Throughout these reactions, the chromophoric character of nitrogen is fully exhibited. Colorific properties are generated by its substitution in intrinsically colourless substances, and these increasingly as the complexity of the substituted compound increases. At the beginning of the series there is the *yellow* and unstable indogenide from acetaldehyde, and, in its culmination, the exceedingly stable and intensely *blue* indigo.

Thus, by cumulative evidence gathered from divergent lines of investigation with wonderful skill, the proposition around which these unique researches centre is left upon an abundantly substantiated experimental basis.

III. SYNTHETIC INDIGO IN ITS RELATION TO THE VEGETABLE PRODUCT.

Vegetable indigo is formed as a glucoside in the cells of plants of the genus *indigofera*, growing in India, Africa, and Central America, in general, in a tropical climate. The Indian crops are of greatest importance both in point of quality and quantity. The seed of the plant is there sown in rudely tilled soil and harvested after a few months, just before the blooming time. Two crops are grown each year. The colouring matter is secreted mainly by the leaves. To prepare it, the green plants are steeped in earthenware or wooden vats in water and allowed to ferment during nine to fifteen hours, according to the temperature. A yellow fluid is formed and run off into a vat, placed conveniently below the first. It is here agitated, to facilitate access of air for oxidation, mechanically or by hand. The fluid soon begins to change colour to green and later blue, with the gradual separation of the colouring matter as a blue precipitate. After clearing, the supernatant fluid is removed and the precipitate transferred to a third vessel, where it is boiled with water for several hours to still fermentation and to some extent purify it. Collection upon filter-cloths, expressing the adhering water, forming by cutting into cubes or lumps, drying, and packing complete the preparation for the market.

Vegetable indigo is not the nearly pure substance represented by its rival, synthetic indigo, but besides contains indirubine, indigo-brown, glutinous substance, ash, and other impurities derived from the mode of preparation. In the adulterated colour, chalk, lime, ashes, and the like are found. The percentage of indigo may vary from 20 to 90 per cent.

The Indian indigo crop for each year from 1879 to the present time is given in the accompanying table.*

The yield for 1898 was 124,580 maunds or 11,012,872 lbs., in value at the average price (*Four. Soc. Dyers and Colourists*, Indigo Chart, Oct., 1898) of 64 c. for that year, nearly 7,050,000 dols. Allowing that the Indian production is five-eighths of the total, and that of other growers proportionally good at the price given, the value of the total yield for 1898 would be about 11,275,000 dols. (Otto N. Witt, *Prometheus*, xi., 371, estimates the value of the world's production of indigo at 15,000,000 dollars).

In competition for this prize, the leading representative of Germany's chemical industry, the great Badische Anilin u. Sodafabrik, has entered with synthetic indigo by processes described or modifications of them. It may not be amiss, particularly at the present juncture in its development, to pause for a moment's consideration of the magnitude of this industrial giant (the data are from 1896). Its products are chiefly the coal-tar colours of

* *Amer. Wool and Cotton Reporter*, Oct. 12, 1899, p. 1209. By the courtesy of Messrs. Kuttroff, Pickhardt, and Co., New York, my attention has been directed to this and other statistical information here reproduced. I am further indebted to the same firm for samples of artificial indigo used in illustration of the lecture.

Year.	Factory maunds.
1879	73,128
1880	136,200
1881	135,405
1882	150,278
1883	159,388
1884	166,507
1885	108,692
1886	131,261
1887	130,825
1888	132,354
1889	144,718
1890	100,733
1891	150,506
1892	87,231
1893	116,329
1894	160,400
1895	162,200
1896	158,800
1897	110,212
1898	124,580

every class, embracing the aniline, alizarine, azo, resorcin, and gallic acid colouring matters. It further manufactures every variety of auxiliary and intermediate product consumed in the above preparations, including all products of the acid, soda, and chlorine industry. It was founded in 1865, and is now situated in Ludwigshafen on the Rhine, opposite Mannheim, one of the most influential commercial centres of Southern Germany, and has branch works in France and Russia. The main concern at Ludwigshafen employs 100 scientifically trained chemists, 30 engineers, and a commercial and accountant force of 230 men. In 1896, including overseers and labourers, the employees of the works numbered about 4800. The factories occupy 210 acres, of which 60 acres are covered by buildings of the works, and 492 dwellings for labourers and 78 for officials. Within its limits there are 21 miles of railway. The consumption of coal yearly is 190,000 tons. For the generation of steam for the heating of apparatus and running 190 steam engines of 6500 horsepower, there are 83 boilers. The water-works of the establishment provide annually 2640 million gallons of water, an ice plant supplies over 13,000 tons of ice, and the gas-works generate nearly 340 million cubic feet of gas. For electric lighting, there are four dynamo-machines of 1000 horse-power supplying current for 6400 incandescent lights and 470 arc lights. There are nearly three acres of shops for repairs of every description and the construction of special apparatus.

This establishment owns the principal and promising patents relating to artificial indigo and intermediate products required in its preparation. In connection with investigators already named, it has, since Baeyer's *o*-nitro-cinnamic acid synthesis, almost incessantly worked upon the problem of rendering methods discussed practicable. Experiments, in the main, have been directed towards a cheapening of the necessary materials and intermediate products. After a period of twenty years, difficulties have been so far overcome that synthetic indigo is an established article of trade, making its appearance somewhat generally first in 1897. Already it is making itself felt by a material reduction in the price of indigo. In April, 1880, the year of Baeyer's first promising synthesis, medium quality of Bengal indigo sold for 1.87 dols. per pound; in December, 1898, one year after the introduction of synthetic indigo, at 87 c. Good medium Kurpah brought 90 c. in January, 1899, and only 62 c. in December, 1898, in the London market. In September of last year the synthetic preparation was quoted at 38 c. in New York (*Oil, Paint, and Drug Reporter*, September, 1899).

When Wöhler discovered a synthesis for urea, nearly seventy five years ago, the tilling of a fertile field in chemical research was begun. One by one a long list of compounds, in Wöhler's time generally regarded as ex-

clusively within the creative power of the vital force resident in the cells of vegetable and animal organisms, has become a proud trophy of searching investigation.

The knowledge acquired by these triumphs over mystery as connected with the animal organism has acted with beneficence upon the development of higher physiology and the science of medicine. By the synthesis of alizarine and indigo, the vegetable world has been invaded with results already prominently presented in the first instance, and those of similar significance are now confidently regarded as fast approaching a brilliant industrial climax for synthetic indigo.

ON THE SYNTHESIS OF COMPLEX EQUATIONS.

By WILLIAM ACKROYD, F.I.C., Public Analyst for Halifax.

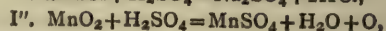
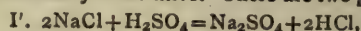
THE regular building up of complex chemical equations receives no attention in text-books. The student is usually left to arrive at an expression of his facts by a series of shots or approximations, or else to commit already constructed equations to memory, to be recalled as required.

Their systematic synthesis appears to the writer of sufficient importance for him to send to the *CHEMICAL NEWS* the following brief notes of the method he has followed for some years with advanced students and to advocate its wider use. It is briefly:—

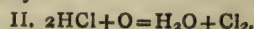
- (1) To select the necessary primary equation or equations;
- (2) To work out the naturally following secondary or tertiary, &c.;
- (3) To cancel common quantities; and
- (4) To add up the results for the final complex equation.

The synthesis of the following—

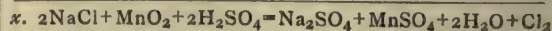
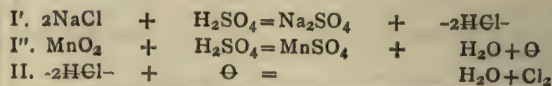
$2\text{NaCl} + 2\text{H}_2\text{SO}_4 + \text{MnO}_2 = \text{Na}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$
will be sufficiently illustrative. There are two primaries—



and one secondary—

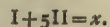


The arrangement of quantities, cancelling of those common to both sides, and the final addition to get the complex equation are as follows:—

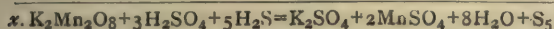
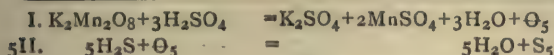


Where the inner nature of this reaction is mentioned, it is usual to suppose that the secondary equation refers to the action of HCl on MnO_2 to liberate the necessary chlorine (*vide* "Reynolds's Experimental Chemistry," 1890, Part II., p. 72), but synthesis on this basis yields contradictory results.

The action of acid (H_2SO_4) permanganate of potash on various reducing agents, such as H_2S , H_2SO_3 , H_2O_2 , FeSO_4 , and KI, may be taken as examples of the system which the method lends itself to; they have one primary equation in common, and are all of the following type:—



The primary equation is the one representing the oxygen available on the action of the acid, and as it is five times that required in the secondary the latter has to be taken five times in the addition, as follows:—



It is unnecessary to proceed with further examples, as the chief interest of the subject to the reader will be in his own application of the synthesis to various complex equations.

ON COMMERCIAL LIQUID CARBONIC ACID.

By J. C. A. SIMON THOMAS.

THE widely different prices charged by various manufacturers of liquid carbonic acid in steel cylinders, for use in ice-making machines on board men-of-war in the Dutch navy, have led me to examine into the purity of the carbonic acid coming from different sources. I have only been able to find two papers on this subject; one a very short one by Fleck (*Vierteljahrschr. Nahrungs und Genussmittel*, 1899, iv., 78), in which the author states that in using ordinary hydrochloric acid which contains arsenic, for preparing the carbonic acid used in breweries, this latter may contain chloride of arsenic; the other, a preliminary communication from Grünhut (*Chem. Zeitung*, 1895, 505 and 555), in which the author gives a method of analysis. Grünhut did not find any gaseous impurities in the three samples he examined. On the other hand, in every case he noticed the presence of organic and reducing matters by passing the gas through sulphuric acid, which was turned brown, and through either acid or alkaline permanganate, which was decolourised after a few hours. These impurities come from the residue which he found in the cylinders after having emptied them of gas. This residue consisted of a thick brown liquid, which contained principally glycerin and oxide of iron. He is of the opinion that the glycerin comes from the compressor, and that in the presence of water and carbonic acid it has dissolved the iron. The author does not give any information with regard to the manner in which the carbonic acid he examined was prepared.

Commercial liquid carbonic acid is prepared in four different manners (*Zeit. für Angewandte Chemie*, 1898, p. 1193): from natural carbonic acid gas which is found in certain volcanic regions; from carbonates of lime or magnesia; by the combustion of coke, according to Ozouf's method; and from the carbonic acid which is formed during fermentation.

The different cylinders of carbonic acid which I have had pass through my hands were from the first three sources. There does not yet appear to be any commercial carbonic acid from fermentation, in Europe at any rate, although I have been told that it is manufactured by Guinness and Co., Dublin.

The general course of the experiments was as follows:—

The first thing to determine was whether the gas which came off contained any gaseous impurities non-absorbable by a solution of soda, and, if such was the case, the nature of these impurities. The gas was then passed through a solution of iodine in iodide of potassium for several hours, for the detection of sulphurous acid, through a solution of acetate of lead for the detection of sulphuretted hydrogen, and, according to Grünhut's method, through concentrated sulphuric acid, and acid and basic solutions of permanganate, to show whether organic impurities were present or not.

I may as well say at once that I have never found either sulphurous or sulphydric acid, nor organic matter, to be present.

After the qualitative, we proceed with the quantitative analysis. The gas is passed into a vessel over mercury, and the carbonic acid absorbed with a solution of soda. The water is estimated as in the preliminary examination, by passing the gas through chloride of calcium or potash

tubes; thus the amounts of carbonic acid and water are determined simultaneously, and the water calculated from these quantities.

The gaseous impurities are carbonic oxide and air, and as, apparently, these gases occur principally in the first portions of carbonic acid that come off, the estimation by means of soda is repeated after the cylinder has been partially emptied. The amount of carbonic acid given off is determined by weighing the cylinder.

Finally, the cylinder is completely emptied, and the nature and quantity of the residue determined.

The results of these analyses are given in the following table:—

No.	Origin of the CO ₂ .	Water per cent.	Gases insoluble in soda. Per cent by volume.	Nature of the gas.
1.	Ozouf's process	0'07	2'0	Air
2.	Natural	0'10	0'8	Air
3.	Magnesite	0'13	4'0	CO
4.	Prepared artificially* ..	0'03	3'4	CO
5.	Carbonaceous rock ..	0'17	5'7	Air

* No more precise data could be obtained.

In the last case the composition of the residual gas was determined by means of pyrogallate of potash, and it was found to consist of 85'1 per cent of nitrogen and 14'9 per cent of oxygen, by volume; it was thus richer in nitrogen than air is.

On repeating the estimation of the gaseous impurities, after having allowed a certain quantity of gas to escape, the following results were obtained:—

No.	Gas given off.	Percentage of gaseous impurities.
1.	Half	Inappreciable
3.	Do.	Do.
4.	90 per cent.	Do.
5.	33 ..	0'8 per cent by volume.

Tube No. 2 was not examined again, as the original proportion was so low.

The amounts of carbonic acid and residue were as follows:—

No.	Contents.	Residue.	Nature of the residue.
1.	10'0 kilos.	0'5 g.m.	Water, with traces of oxide of iron in suspension.
2.	10'3 "	520'0 grms.	517 grms. of water and 3 grms. of oxide of iron.
3.	10'1 "	1'0 g.m.	Water, with traces of oxide of iron in suspension.
4.	8'0 "	0'0 "	—
5.	9'9 "	8'5 grms.	Water, with traces of oxide of iron in suspension.

We see, from these analyses, that the purity of commercial carbonic acid is very satisfactory. The proportion of water in the gas which comes off in the first place is negligible. The gaseous impurities are of more importance: from this point of view the natural gas is the purest, but in the others the total amount is low, and should not exceed half the figures given, since, when the cylinders are half empty, we can no longer determine the amount present. The presence of carbonic oxide in the gas made from magnesite seems to indicate that it was not prepared only by the use of acid, but also by heating the mineral, and that the carbonic oxide is formed in the presence of reducing materials. The carbonic oxide is to be reckoned with when the carbonic acid is for use in ice-making machines on board men-of-war, these machines being liable to leak especially when first put to work, and the space in which they are used is very restricted. I have therefore advised that the carbonic acid must be free from carbonic oxide; it should not, in fact, contain any other impurity than air. The residue was not of any importance, except in the case of the natural gas (5 per cent by weight); in the other cases it does not exceed 0'1 per cent. I cannot give any other reason for the high proportion of water in the natural gas than that given by the maker, viz., that during the manufacture of mineral

waters a certain quantity of water enters the cylinders, and care should be taken to empty this out each time they are used. — *Zeitschrift für Angewandte Chemie*, April 17, 1900.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

There has been very little rain at Oxford during the month, the total fall being only 0.88 inch, distributed over ten days. The average fall being 2.68 inches, we have a deficit of 1.80 inches for the month. This cancels the previous excess of 0.96 inch for the year and gives instead a deficit of 0.84 inch, or 6.1 per cent on the thirty years' average.

Our bacteriological examinations of 520 samples have given the results recorded in the following table; we have also examined 36 other samples, from special standpipes, &c., making a total of 556 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	299
New River, filtered (mean of 132 samples) ..	11
Thames, unfiltered (mean of 26 samples) ..	1338
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 274 samples) ..	25
Ditto ditto highest	250
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	450
River Lea, from the East London Company's clear-water wells (mean of 38 samples) ..	19

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

Contribution to the Study of Roumanian Petroleum.—L. Edeleanu and G. A. Filiti.—The authors divide their subject into two parts. In the first part they describe the chemical examination, showing the true nature of the raw petroleum by the determination of the constitution of the bodies of which they are formed. In the second part they show the physical and technical properties, which are of such importance in the industry of petroleum refining.—*Bull. Soc. Chim.*, xxiii., No. 10.

NOTICES OF BOOKS.

The Oil-Chemists' Handbook. By ERASTUS HOPKINS. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1900. Pp. 72. 8vo.

THE author of this volume holds the position of chemist in charge of United States laboratories at Boston, and has had many years' practical experience as an oil-chemist. As stated in the introduction, the handbook is intended to contain not only the methods used in testing and analysing oils, but also the analytical data for identifying unknown oils and for detecting adulterants. The small number of pages in the book gives to those who have not examined it no idea of the immense amount of information it contains; besides the 72 numbered pages there are many folding tables in which practical data are closely packed. For instance, the "Table of the Chemical and Physical Constants of Oils and Fats" has six openings, each about two feet long, ruled in sixteen columns. The position of the oils in the various tables is determined by the numerical value of the constants; thus in the table of iodine absorption constants, sardine-oil stands first, while in the table of acetyl values castor-oil heads the list. This arrangement is intended to facilitate the identification of an unknown oil. References to journal-literature are freely given. The author uses the objectionable word "titer," and writes benzol for benzene. The book will be welcomed by all engaged in testing oils. There are illustrations and an index.

Air, Water, and Food, from a Sanitary Standpoint. By ELLEN H. RICHARDS and ALPHEUS G. WOODMAN. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1900. Pp. 226. 8vo.

MRS. RICHARDS, who is Instructor in Sanitary Chemistry at the Massachusetts Institute of Technology, Boston, is already known to readers of the *CHEMICAL NEWS* by her earlier works: "Plain Words about Food," "Home Sanitation," "Food Materials and their Adulterations," "The Chemistry of Cooking and Cleaning," and "The Cost of Living as Modified by Sanitary Science." These volumes show that the busy author has long devoted her energies to the study of the three essentials for healthful human life; it is gratifying to note that her experience has made her hopeful for the future, for she writes:—

"The day is not far distant when a city will be held as responsible for the purity of the air in its school-houses, the cleanliness of its water in its reservoirs, and the reliability of the food sold in its markets as it now is for the condition of its streets and bridges; nor will the years be many before educational institutions will be held as responsible for the condition of the bodies as of the minds of the pupils committed to their charge; when a Chair of Sanitary Science will be considered as important as a Chair of Greek or of Mathematics; when the competency of the food-purveyor will have as much weight with intelligent patrons as the scholarly reputation of any member of the faculty."

The book under review contains, besides discussions of the characteristics of pure air, safe water, and wholesome food, instructions for securing them under many conditions, for proving them, and for detecting the commoner sophistications of the latter. In the chapters on Air and Ventilation, the author describes the methods of determining carbon dioxide in the atmosphere devised by Pettenkofer, by Cohen and Appleyard, by Fitz, and by Wolpert. The chapters on Water are written from the standpoint both of the householder and of the chemist, and contains much practical information. These are followed by a chapter giving methods for determining free and albumenoid ammonia, the total organic nitrogen, the carbonaceous matter, the chlorine, the dissolved oxygen, the hardness, &c. The chapters on Food in Relation to

Human Life, and the Problem of Safe Food, show the familiarity with the subjects that might be expected of the author; but she treats the analysis of milk, butter, cereals, and fermented liquors rather cursorily.

In the Appendix are useful tables and a list of books relating to the topics treated, chiefly in English. There is an index. The book will be found valuable as an educational factor in laboratory training, and as a handbook in the workshop of the analytical chemist called on to make examinations of air, water, and food.

H. C. B.

Commercial Organic Analysis. By ALFRED H. ALLEN, F.I.C., F.C.S., &c. Third Edition, with Revisions and Additions by the Author and HENRY LEFFMANN, M.A., M.D. Volume II., Part II. London: J. and A. Churchill. 1900. Pp. 330.

THE present volume completes the revision of volume II. of this work, with the exception of the section relating to essential oils. It deals with the hydrocarbons, petroleum and coal-tar products, asphalt, phenols, and creosotes.

The original second volume, dealing with oils of all kinds, consisted of 573 pages. It has now been split up into three Parts. Part I. was published in 1899 (see CHEM. NEWS, vol. lxxix., p. 225), Part II. is now before us, and Part III., which will treat of the essential oils, aromatic acids, camphors, resins, and balsams, is now ready for the printer. The two parts already issued cover over 700 pages, so it will be seen that a large amount of matter has been added.

The principal additions and changes herein made are:—The systematic arrangement of the hydrocarbons according to the modern system, including the application of the nomenclature of the Geneva convention—this is a heavy task in itself; we also find summaries of the technology of acetylene, coke-oven tar, and asphalt; the testing of petroleum, lubricating oils, and coal-tar products, and special tests for many benzene derivatives now used as drugs, food-preservatives, or disinfectants. A large addition has also been made to the analytical data concerning phenol, phenolic disinfecting agents, and wood-tar creosote.

The reviser has added, as an Appendix, a detailed description of new extracting and drying apparatus, and has calculated tables of comparison of Beaumé degrees and specific gravities lighter than water. The Index, which is always an important feature in a book of this class, has been much enlarged, and makes a worthy ending to an excellent work.

The Chemistry of Fire and Fire Prevention. By HERBERT INGLE, F.I.C., F.C.S., and HARRY INGLE, Ph.D. (Munich), B.Sc. (Victoria). London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1900. Pp. 287.

THE present work, intended more especially for the use of Insurance Surveyors, Works' Managers, and those interested in fire risks and their diminution, is based upon two courses of lectures delivered by one of the authors; these lectures, considerably extended and re-arranged, are now published in this volume.

On looking through the book it will soon be seen that the title is to a certain extent misleading; the Chemistry of Fire occupies only a small portion, principally in Chapter I., while the part devoted to fire prevention and extinction (Chapter XV.) is not much larger. The intervening chapters deal with a variety of subjects, such as the preparation and purification of coal-gas; fuel; illuminants; oils; volatile solvents and coal-tar products; paint- and varnish-making; textile manufactures, &c. In all these chapters the possible dangers of fire are pointed out, but the general impression left is more that of a work on chemical technology.

A very convenient innovation worth noting is, that the

heading of every left-hand page gives the number of the chapter as well as the subject.

The Cyanide Process of Gold Extraction. A Text-book for the Use of Mining Students, Metallurgists, and Cyanide Operators. By JAMES PARK, F.R.G.S., &c. First English Edition, Revised and Enlarged from the Third Edition published in New Zealand. London: C. Griffin and Co., Ltd. 1900. Pp. 127.

OF late years the application of scientific investigations and methods to the treatment of ores has rendered metallurgy more and more dependent on chemical knowledge, and in no department is this more striking than in the cyanide process of gold extraction. Quite recently wet-crushing and cyanide treatment have largely superseded dry-crushing and direct cyaniding in New Zealand, and in every case the change has been attended with complete success. The results obtained with these comparatively complex ores are of very great interest, and have been embodied by the author in a separate appendix.

The fact that gold and silver are soluble in solutions of alkaline cyanides has long been known, but the discovery that the solution must be *dilute* is comparatively modern, and is one of the most important facts in the application of this process to successful gold extraction on a large scale.

No hard and fast rules can be followed in the working of the cyanide process, as modifications have to be made to meet the special requirements of the different classes of ores and tailings; but the essential features of the process are practically the same in all cyanide plants, and may be summarised as follows:—1. Filling the leaching vats. 2. Preliminary treatment with water or alkaline washes if necessary, to remove the mineral salts and acids, in the case of an acid ore, which would decompose the cyanide solutions. 3. Leaching with what is called the "strong" solution of cyanide: this, however, should only contain from 0.3 to 0.6 per cent of KCy. 4. First wash with cyanide from "strong" sump, containing 0.1 to 0.25 per cent of KCy. 5. Second, wash with cyanide from "weak" sump, containing from 0.02 to 0.1 per cent of KCy. 6 and 7. Same as last. 8. Washing with clean water. The cyanide solutions are then allowed to flow through the zinc extraction boxes, where the gold is deposited in the form of a black powder or mud; this is then smelted and cast into ingots. The above process is generally known as the McArthur-Forrest process, and is most successful in the treatment of ores in which the gold occurs in a very finely-divided state, and in which the quantity of base minerals or metallic salts, destructive to cyanide, is small.

Since the introduction of the cyanide process, the precipitation of the gold by metallic zinc has always been regarded as a weak point, and much time has been spent in the endeavour to find a substitute for it. Electrical precipitation naturally engaged a good deal of attention, but it was found that the precipitation of the gold from weak solutions was accompanied by the decomposition of the water. In the Siemens-Halske process this difficulty is overcome by causing a slow artificial circulation of the cyanide solution in the extractor: this method has been successfully introduced in a number of mines in the Witwatersrandt gold-fields, and was, before the war, already becoming a formidable rival to the McArthur-Forrest zinc-precipitation process.

Other cyanide processes which may be mentioned are the Hannay electro-cyanide method, by which the whole of the gold is obtained as an amalgam; the Park-Whitaker cyanide process, intended for the treatment of cupriferous ores and concentrates, which are first subjected to a chloridising roasting,—after this the soluble copper chlorides are removed by leaching with water; an alkaline wash is then applied, and the gold and silver extracted with a dilute solution of cyanide. In the Sulman-Teed process cy-

anogen bromide, or some other halogen compound of cyanogen, is used as the solvent in conjunction with zinc as a precipitant; the process is claimed to be well adapted for the treatment of pyritic concentrates and complex ores.

We can strongly recommend this book to all those engaged in gold and silver mining: there will no doubt be a very large extension of mining operations when the pacification of the Transvaal has been completed, and the demand for really skilled managers and metallurgists will be greater than it has ever been before. The author is a thoroughly practical man, and has handled the subject in a clear and practical manner, while at the same time the theoretical side of the question has not been neglected.

CORRESPONDENCE.

ACTION OF SULPHUR CHLORIDE ON OILS.

To the Editor of the Chemical News.

SIR,—In a work, "Le Caoutchouc et la Gutta Percha," by Seeligmann and others, I note, at page 279, the following extraordinary statements, due to Henriquez, on the authority of the CHEMICAL NEWS (1888, p. 113):—

"Warren pretend que les huiles siccatives donnent avec la chlorure de soufre des masses solides, insolubles dans le sulfure de carbone, tandis que les huiles non siccatives donnent des produits solubles dans ce véhicule. Stolmann, dans la dernière édition du Dictionnaire du Muspratt, écrit que ces résultats semblent mériter peu de créance, puisque l'on sait que l'huile d'olives, type des huiles non siccatives, se transforme, sous l'action de chlorure de soufre, en une masse analogue au caoutchouc, insoluble dans l'éther. Les faits signalés dans le brevet de Sommers, ainsi que nos expériences personnelles, contredisent formellement les assertions de Warren."

I cannot find that the article in CHEMICAL NEWS contains anything to justify the conclusion that olive oil in particular does not give a product different to many other oils which are regarded as non-drying, as olive oil, castor oil, almond oil, cotton oil, &c.

In fact, the conclusion I came to when the article was written, was that the division of oils into drying and non-drying oils was of technical use to a painter, and as a scientific distinction could not be recognised.

This work of Seeligmann should be of use to your readers who are interested in indiarubber and gutta-percha. It can be obtained at 30, Rue des Dragon, Paris.—I am, &c.,

THOMAS T. P. BRUCE WARREN.

Tamworth Villa,
Earlham Grove, Forest Gate.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

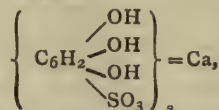
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 8, August 20, 1900.

Extraction of the Oxygen of the Air by means of Solution at a Low Temperature.—Georges Claude.—The author's experiments had for their object the production of an air containing 50 or 60 per cent of oxygen, at a comparatively small cost, such a gas being sufficient for most purposes where the use of oxygen is necessary. The method employed consisted in saturating a quantity of certain liquids at a known pressure and temperature with oxygen, and then extracting the gas by lowering the

pressure. The author used several alcohols and ethers, besides acetone, acetol, chloroform, liquid methyl oxide, petrols, benzine, liquid chlorine, and different inorganic liquids. The results obtained are not entirely satisfactory, but the research is being continued.

Pyrogallol-Sulphonic Acids.—Marcel Delage.—By the action of sulphuric acid on pyrogallol, and purification of the products obtained, the author prepared a calcium salt of pyrogallol-sulphonic acid, in the form of large and small crystals. Both these sets of crystals dried at 110° correspond to the formula—



the experimental numbers closely approaching those of theory. The barium salt has also been obtained, and also the pyrogallol-monosulphonates of potassium, sodium, and ammonium.

The Dextrines of Saccharification.—P. Petit.—The author prepares the dextrines which are formed during saccharification of a starch sediment at 50°, 60°, and 70°, the action being stopped by a rapid heating, after which iodine ceases to produce a colouration.

The Employment of Sodium Dioxide to Purify Wells Contaminated by Carbonic Acid.—E. Derennes.—Several methods of removing the carbonic acid from wells have been tried, all more or less awkward. The use of sodium dioxide seems to solve the problem. The CO₂ is absorbed, and is replaced by an equal volume of oxygen, the air returning to its normal composition.

Nos. 9 and 10.

These two numbers contain no matter of chemical interest.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxiii., No. 10.

Action of Hydrogen on Sulphide of Antimony.—H. Pélabon.—Already noticed.

Selenide of Zinc and its Dimorphism.—M. Fonzen-Diacon.—Already noticed.

New Preparations of some Oxides of Uranium.—J. Aloy.—Already inserted in full.

On the Cyclic β-Diketones.—M. Georges Leser.—There is at present no general method for the preparation of these bodies, of which three only are yet known. The first two were prepared by Ad. von Baeyer (*Berichte*, xxx., 28) from the ketonic acids of menthone and tetrahydrocarvone; they are pentagonal. The author has prepared the third (*Bull. Soc. Chim.*, xxi., 546) by the isomerisation of acetylmethylheptenone. These three diketones have some common properties, but they have also differences which must not be overlooked. The first two form a salt of copper, and become hydrolysed quantitatively on contact with the alkalis, re-forming the original ketonic acids; the third only undergoes this hydrolysis partially, and a secondary reaction intervenes; it does not give a copper salt. In the endeavour to find a reason for these differences, the author has succeeded in reproducing a certain number of these bodies, and in applying Claisen's reaction to the cyclamones. Wallach's methylcyclohexanone being easy to prepare, and the author here describes the method applied to this ketone.

The Dichlorised Phthalic Acids, Products of Condensation.—E. C. Severin.—A long paper not suitable for abstraction.

Estimation of Chlorine in Gastric Juice.—G. Meillère.—The estimation of chlorine in gastric juice comprises the following operations:—(1) Preliminary filtration or centrifugation of the liquid for the subsequent

examination of the deposit. (2) Determination of the acidity on 10—20 c.c. by means of a titrated solution of baryta in the presence of phthalein. The result is calculated as HCl; it is convenient to also express it in cubic centimetres of normal solution. (3) The total chlorine: 10 c.c. of the juice, containing a slight excess of carbonate of lime, are treated with 20 to 50 centigrams. of nitrate of lime (according to the richness of the juice in organic matters), and evaporated to dryness, then gently ignited until the carbon has disappeared. The residue is taken up with a little distilled water containing a few drops of acetic acid; a little chalk and a drop of potassic chromate are added, and the liquor is then titrated with nitrate of silver. (4) Chlorine in the dry residue. This residue is best prepared in vacuo, and the operation proceeded with as in the case of the total chlorine. (5) Chlorine in the ash. Ten c.c. of the juice are evaporated and gently ignited without the addition of any other body, and the operation completed as above. The results are calculated as HCl.

Chemical Analysis of the Mineral Water from the Cold or Park Spring at Evaux-les-Bains (Creuse).—E. Bonjean.

Analysis of the Natural Mineral Water from the No. 3 Spring, Brault Sail-sous-Couzan (Loire).—E. Bonjean.—Both the above papers have been inserted in full.

New Method for the Estimation of Fats in Dairy Products.—M. Lindet.—This method of estimating the fatty matters in milk and cheese is based on the solubility of casein in a concentrated solution of resorcin. The apparatus designed for effecting this analysis consists of a cylindrical glass bulb, having a capacity of 15 grms. for milk analysis, and 18 to 20 grms. for cheese; it is closed at one end with an indiarubber stopper, through which a glass rod passes; the other end terminates with a narrow graduated tube, the special calibration and use of which is fully described. When in use this apparatus is placed vertically with the graduated tube downwards; this tube is plugged and filled with mercury to prevent the casein entering and making it dirty. Five grms. of resorcin, 5 c.c. of milk, 2 drops of soda at 36°, and 1 drop of solution of a colouring material are introduced; the stopper is then fixed in firmly, and the whole apparatus turned upside down to allow the mercury to fall out of the graduated end, which is then unplugged; it is then placed in a water-bath of sufficient depth for the graduated tube to be almost entirely immersed in the boiling water. The casein dissolves rapidly, especially if the apparatus is shaken, which must be done with care. It is left in the water-bath until the level of the butyrous layer does not alter after two readings made at an interval of ten minutes. The operation lasts half-an-hour. The results obtained are identical with those given by exhausting with ether. The estimation of the fatty matter in cheese is even more simple, and the separation of the two layers is done more easily. One gm. of cheese, about 15 c.c. of a warm solution of 100 grms. of resorcin in 100 c.c. of water are placed in the apparatus, which is then reversed and treated as before. The operation lasts from ten to fifteen minutes. If it is desired to estimate the fatty matters in cream, it is only necessary to dilute the cream with the quantity of water necessary to bring it to the original strength of the milk.

MISCELLANEOUS.

Schools of Chemistry.—The following additional information of interest to Students has been received:—

THE BIRKBECK INSTITUTION, Breams Buildings, Chancery Lane.—This Institution, which has now completed 77 years of educational work in the metropolis, commences its new Session on Monday, October 1st. There

are both day and evening courses of study, which comprise the various branches of Natural Science, Mathematics, classical and modern Languages, Economics, Commercial Subjects, Law, Mental Science, Music, and Art. The courses provide for the Examinations of the University of London, in the faculties of Arts, Science, and Commerce, those of the Conjoint Board, Civil Service, &c. The Report for the last Session shows that during the year fifty Students passed some university examination, while large numbers gained successes at various public examinations. The Institution has had many additions to its appliances in recent years, and the Physical, Chemical, and Metallurgical Laboratories are now very thoroughly equipped. The day classes provide courses in Chemistry, Biology, Physics, and Mathematics, for the Science Degrees of London University. There are also day classes in Languages, Music, and Shorthand. The School of Art is open both day and evening. During the recess, considerable additions and improvements have been made by the aid of a gift of 2000 guineas from Mr. F. Ravenscroft to commemorate his completion of a membership of fifty years. A new reading room, a new magazine room, and a social room have been provided, and a well-appointed Metallurgical laboratory has been added. The Calendar supplies complete syllabuses of the classes and full information about the Institution. A popular Lecture or Entertainment is given in the Theatre every Wednesday evening.

CHARTERHOUSE (WILLIAM ROGERS' MEMORIAL) SCIENCE SCHOOLS AND LITERARY INSTITUTE.—The Winter Session will commence Sept. 29th. During the late Session a large number of Students, mostly Elementary Teachers, availed themselves of the privileges afforded by this Institute. Instruction of a practical character is given in most of the Sciences at a nominal fee. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) can work in a well-fitted Laboratory. Aspirants for University Honours can, at a small expense, be assisted in their studies. Special opportunities for the study of Hygiene will be afforded this Session to Laundry and Cookery Students who desire to be qualified for London School Board and L.C.C. appointments. Full particulars of the classes can be obtained from C. Smith.

CHEMICAL DEPARTMENT, MIDDLESEX HOSPITAL MEDICAL SCHOOL.—Lecturer, A. M. Kellas, B.Sc., Ph.D.; Demonstrator, W. G. Taylor. The Chemical Department opened Sept. 25th. Two complete courses of Lectures and practical work are given for the Conjoint Board Examination (R.C.S. and R.C.P.), starting in October and May respectively. A complete course of practical and theoretical work for the Inter M.B. of London University starts in January and continues to beginning of July. Two courses of Toxicology for the M.B. of London are given annually, commencing in September and July respectively. Courses of Chemistry for the Diploma of Public Health—Conjoint Board or Cambridge—can be started at any time throughout the Session, and hours can usually be arranged to suit the convenience of candidates. The Bacteriology in connection with this course is given by A. G. R. Foulerton, F.R.C.S., D.P.H.

THE MUNICIPAL TECHNICAL SCHOOL, Princess Street, Manchester.—The new School now in course of completion will be opened in September, 1901. In addition to the ample arrangements provided for Industrial Chemistry, the Committee have decided upon the erection of new building, 1248 square yards in area, for Bleaching, Dyeing, Printing, and Finishing Textile Goods. The new School, it is stated, will be the largest and probably the most completely equipped school in the kingdom.

HARTLEY COLLEGE, SOUTHAMPTON.—Principal, R. Wallace Stewart, D.Sc. (Lond.). London University Courses in Arts and Science, Science Courses for Medical and Dental Students, Mechanical and Electrical Engineering Courses,

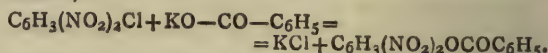
READING COLLEGE.—Lecturer in Chemistry, C. M. Luxmoore, D.Sc., F.I.C.; Assistant, J. L. E. Drugman, Ph.D.; Demonstrator, W. J. Monk. The Autumn Term begins Thursday, October 4th. The following are the Courses of Instruction in Chemistry:—I. Elementary Course (Autumn Term only), Tuesdays and Thursdays; fee £1 1s., or, including laboratory instruction, £2 12s. 6d. II. First Year Course, Tuesdays and Thursdays. III. Second Year Course, Wednesdays and Saturdays. IV. Advanced Course. V. Agricultural Chemistry, Mondays and Fridays. The Fees for the above, including Laboratory Instruction, are—Term, £4 4s.; Session, £8 8s. VI. Elementary Chemistry for Agricultural and Horticultural Certificate Students, Mondays; fee, £1 1s. VII. Pharmaceutical Chemistry. VIII. Pharmacy. IX. Laboratory work, daily; Fee, term, £3 3s. Special course of studies in Pharmacy. Special class for Teachers in Elementary Schools. Evening classes in Chemistry, Physics, and other Science subjects. The Diploma of Associate of Reading College in Letters and Science is awarded to Students who attend a full course of instruction during two Sessions, and pass specified Examinations. Full particulars of subjects of study and other information will be found in the College Calendar, to be obtained, post free 1s., from the Registrar.

INSTITUTE OF PUBLIC HEALTH AND TECHNOLOGY, Seymour House, Old Trafford, Manchester.—Principals, Charles Estcourt, F.I.C., F.C.S., &c., and Philip Anderson Estcourt, Ph.D. The course of instruction is especially intended for those who require a knowledge of Chemistry and Bacteriology bearing upon Sanitary matters. Chemical Technology is specially taught with a view to enable Medical Men and others engaged in Sanitary matters to understand the operations at the various works which may come under their control. Persons who desire to take up the branch of Chemical Engineering, including Electrical Engineering, will also have special opportunities of pursuing such studies.

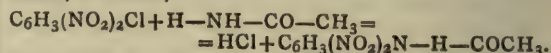
UNIVERSITY COLLEGE, SHEFFIELD.—*Department of Metallurgy.* Professor, J. O. Arnold; Lecturer, A. McWilliam, A.R.S.M.; Demonstrator and Lecturer on Fuel, F. K. Knowles; Demonstrator of Micrographic Analysis, F. Ibbotson, B.Sc. This Department has been equipped with a view to thoroughly meeting the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

CHEMICAL LABORATORY SCHOOL OF MEDICINE, 4, Lindsay Place, Edinburgh.—Practical Chemistry for Medical Science, Technical and Public Health Students. The Course qualifies for graduation at various Universities and the Royal Colleges. Specially equipped for Public Health Chemistry and Bacteriology, and the Technology of Paper-making. Prospectus from Mr. G. H. Gemmell, F.I.C., F.C.S., at the Laboratory.

Action of Chlordinitrobenzene on Benzoate of Potassium and on Acetamide.—O. Kym.—Alcoholic solutions of chlordinitrobenzene and of benzoate of potassium do not react on one another, either in the cold or when heated. If, however, we mix chlordinitrobenzene with benzoate of potassium in the powdered state, and heat the mixture to 180° on an oil-bath, a reaction takes place, and the dinitrophenylic ether of benzoic acid is formed,—



The ether in question melts at 132°; it is identical with that obtained by heating together dinitrophenol and chloride of benzoyl. Acetamide and chlordinitrobenzene also do not react on each other in alcoholic solution, either in the cold or when heated. When heated in the solid state for ten hours in an oil-bath at 200–210°, they give a large quantity of dinitraniline, with a return of 93 per cent of the amount of chlordinitrobenzene used. Acetyldinitraniline, which is saponified during the reaction, is formed,—



The author added acetate of sodium to the fused product, with the object of preventing the saponification of the acetyldinitraniline, but in this case he obtained dinitrophenol. This reaction may be explained by the supposition that dinitraniline is also formed, but that this latter has been transformed into dinitrophenol by the decomposed acetate of sodium, which acts as the carbonate. Chlordinitrobenzene heated with acetate of sodium alone gives rise to the formation of traces of dinitrophenol only.—*Berichte*, xxxii., 3539.

TO LIME MERCHANTS, MANUFACTURING CHEMISTS, and OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the Supply of—

- (a) 22,800 Tons of LIME and
- (b) 5300 Tons of PROTO-SULPHATE OF IRON (Commercial Green Vitriol)

to the Barking Outfall Works, near Beckton, North Woolwich, and Crossness Outfall Works, near Erith, Kent; and

- (c) 25 Tons of CAUSTIC SODA (76 per cent strength) to the Abbey Mills Pumping Station, Stratford, West Ham, E.

Forms of Tenders and other particulars may be obtained at the Engineer's Department at the County Hall, Spring Gardens, S.W.

Tenders, which must be upon the Official Printed Forms and comply with the instructions contained therein or be rejected, are to be delivered at the County Hall, in a sealed cover addressed to the Clerk of the London County Council, not later than 10 o'clock a.m. on Tuesday, October 9th, in the cases of (a) and (b); and Thursday, October 4th, in the case of (c).

The Council does not bind itself to accept the lowest or any tender, and it will not accept the tender of any person or firm who shall on any previous occasion have withdrawn a tender after the same has been opened, unless the reasons for the withdrawal were satisfactory to the Council.

Spring Gardens, S.W.,
September 24, 1900.

C. J. STEWART,
Clerk of the Council.

MR. J. G. LORRAIN, M.I.E.E., M.I.M.E., M.S.C.I.,
Fellow of the Chartered Institute of Patent Agents,
NORFOLK HOUSE, NORFOLK STREET, LONDON, W.C.
"PATENTEE'S HANDBOOK" Post Free on application.

THE CHEMICAL NEWS.

VOL. LXXXII., No. 2132.

SOME RECENT WORK ON THE DIFFUSION OF GASES AND LIQUIDS.*

By HORACE T. BROWN, LL.D., F.R.S.

THE author's recent work, in conjunction with Mr. F. Escombe, on the fixation of carbon by green plants from the carbon dioxide of the atmosphere, necessitated a re-examination of the process of *static diffusion* from a somewhat new standpoint, and in the course of the experiments some new and interesting facts were brought to light which have an important bearing on the laws of diffusion of gases and liquids.

In the case of carbon dioxide and air the absolute rate of the inter-penetration of one gas by the other has hitherto only been determined for high ratios of mixture, but it would be manifestly unsafe to apply the values of such coefficients to the static diffusion of atmospheric carbon dioxide, which only exists in the air to the extent of 0.03 per cent by volume. An attempt was consequently made to determine the coefficient of diffusivity of atmospheric carbon dioxide by a process of static diffusion.

If we imagine a vertical cylinder to be filled with atmospheric air containing the normal amount of carbon dioxide, and regard any plane surface within the enclosed air, it follows, from the kinetic theory, that in any given time the same average number of carbon dioxide molecules will cross this plane in opposite directions, and there will consequently be no change in the average distribution of the molecules throughout the cylinder. If, however, we imagine the bottom of the cylinder to become suddenly capable of absorbing carbon dioxide, say by the introduction of a layer of a solution of caustic alkali, then the molecules of this gas which strike the bottom of the cylinder will be wholly or partially trapped, and in the first brief interval of time a very thin stratum of air, parallel to and immediately above the absorbing surface, will be partially depleted of its carbon dioxide. If we now further consider the interchange of carbon dioxide molecules taking place between this partially depleted layer and the one above it, it is evident that now in a given interval of time a larger number of the molecules must pass from the higher to the lower stratum than from the lower to the higher; the "balance of exchange" will consequently be in favour of the lower layer. This is a condition which will be rapidly propagated from below upwards, and, providing the air outside the cylinder is maintained of uniform composition, a *static condition* will be established in the column. When this condition has been reached, the uncompensated balance of exchange between any two contiguous layers will constitute a steady *flux* or *drift* of carbon dioxide from the outer air to the absorbent surface, the rate of which, if the surface is perfectly absorbent, will be conditioned solely by the diffusivity of the gas. The question from the mathematical standpoint can now be treated in exactly the same manner as the "flow" of heat in a bar after the permanent state has been reached, or the "flow" of electricity between any two regions of a conductor maintained at a constant difference of potential.

The diffusivity of atmospheric carbon dioxide has been determined on these lines by the author and Mr. Escombe, and has been found to have a mean value in C.G.S. units of 0.157. It is pointed out, however, that the difficulties of eliminating all disturbing causes are very great, but

that the experiments suffice to show that the inter-diffusivity of carbon dioxide and air in the ratio of mixture in which they occur in the atmosphere does not materially depart from the value obtained by Loschmidt and others with much higher ratios of mixture. Another and more accurate method subsequently described confirms this conclusion.

An account is then given of the author's researches on the diffusion of gases and liquids through apertures in a diaphragm.

If a condition of static flow of atmospheric carbon dioxide is established down a short column of air, towards a perfectly absorbent surface, the rapidity of flow, conditioned by the diffusivity of the gas, is strictly proportional to the area of the cross section of the column. If, however, we partially obstruct the open end of the column with a diaphragm pierced with a single central aperture, or if we introduce such a diaphragm anywhere in the line of flow, diffusion is modified in a remarkable and unexpected manner.

As the aperture in the septum is gradually reduced in size, the flow through unit area is accelerated, and when the rim around the hole has a breadth of two or three times the diameter of the aperture, this acceleration is found to vary inversely as the diameters of the opening. In other words, the amount of flow then becomes directly proportional to the *linear dimensions* of the opening.

The same fact was also shown to hold good for the diffusivity of aqueous vapour in air, either by the static diffusion of the vapour down a column of air, or by the evaporation from dishes which were covered by thin plates of mica perforated with holes of a definite size. The "diameter law" was also proved for diffusible salts in solution in a somewhat similar manner, the mobility of the liquid being destroyed by using a small percentage of gelatine.

When a solution of caustic alkali is exposed to air which is in slight motion, the amount of carbon dioxide absorbed in a given time is proportional to the *areas* of the surface exposed; but if the liquid surface is surrounded with a broad rim in the same plane, and precautions are taken to prevent air-currents, it is then found that absorption takes place proportionately more rapidly with the small discs of liquid. When extreme precautions are taken, and comparatively small surfaces are employed, a very near approach to the "diameter law" can be attained, but it is more difficult to obtain this result with plane absorbent surfaces than it is with apertures in a septum, for reasons which will be seen later.

The explanation of the phenomena so far described is as follows:—

If we consider the simple case of a circular disc of liquid, surrounded by a broad rim and capable of absorbing carbon dioxide, when such a disc is exposed to perfectly still air, the convergent lines of carbon dioxide will creep through the air towards the disc, establishing a steady gradient of density, and this creep will be a flux perpendicular to the lines of equal density, which will thus form curved surfaces or "shells" surrounding the disc and terminating in the rim. The case is analogous to that of an *electric field* in the neighbourhood of a conductor, having the same shape and dimensions as the absorbent disc. The curves or "shells" of the gas of equal density are the analogues of the similarly curved lines of *equi-potential* above the surface of the electrified disc, while the converging lines of creep or flux of the gas are the analogues of the *lines* or *tubes of force*. The partial pressure of the carbon dioxide in the shells of equal density must vary from *zero* at the absorbent surface to a density corresponding to the maximum pressure of the carbon dioxide in the atmosphere, a point which is theoretically at an infinite distance, but which is practically reached at a distance of five or six times the diameter of the disc. From these considerations it follows that the gradient of density, on which the diffusive flow depends,

* Abstract of a Paper read before the British Association (Section B), Bradford Meeting, 1900.

must vary inversely as the diameters of the discs, and that the absorbing power of the discs will vary directly with their linear dimensions, a deduction which is completely verified by experiment.

In the case of a diffusive flow through a circular aperture in a diaphragm, the hyperbolic lines of flow, which are *convergent* as they approach the aperture, bend round their foci situated in its edges, and form a *divergent* system on the other side. On the inner side of the diaphragm there is produced a system of density shells similar to those outside, but with the gradient of density in the contrary direction. This system of shells is termed *negative*, and is as effective as the outer *positive* system in regulating the flow according to the diameter law, so that this law still holds good even if the outer air-currents are sufficient to sweep away the external positive shells completely. This fact explains why it is easier to obtain a demonstration of the "diameter law" by diffusion through apertures than by diffusion into an absorptive disc formed by a solution of caustic alkali.

By diffusing colouring matter through apertures in a diaphragm the "density shells" can be rendered visible, and it may be shown that their ellipsoidal form is exactly that which is demanded by the above hypothesis.

Simple mathematical expressions were given for all the possible cases of diffusion through apertures in thin plates, and in plates of a sufficient thickness to constitute tubes.

Diffusion through multi-perforate diaphragms was next considered, the septa employed being thin celluloid plates pierced with small circular holes of a determinate diameter.

Such septa produce a local disturbance and intensification of the gradient of density in their immediate neighbourhood, so that the velocity of the flux increases as the obstruction is reached, and decreases again when this is passed. The result of this is that it is found possible to perforate a thin plate with a series of very small holes in such a manner as to exercise but little obstruction when it is interposed in a line of diffusive flow, although the aggregate area of the small holes may represent only a small fraction of the total area of the septum. Examples were given, and also formulæ for the calculation of the amount of resistance produced by a septum of a given thickness and perforated with holes of a definite size and distribution. The diffusive flow observed experimentally under these conditions is in close accord with that demanded by theory.

This method of diffusion through apertures affords a new and apparently accurate method of determining *coefficients of diffusivity*. The author and Mr. Escombe have, up to the present time, applied it to the cases of atmospheric carbon dioxide, aqueous vapour, and solutions of sodium chloride.

ON THE DISTRIBUTION OF CHLORINE IN WEST YORKSHIRE.*

By WILLIAM ACKROYD, F.I.C., Public Analyst for Halifax.

THE present observations are to be regarded as the preliminaries to an attempt to construct isochlores for this part of Yorkshire. The subject is one of acknowledged importance. Prof. Mason remarking:—"State maps, such as those issued for the States of Massachusetts and Connecticut, are most valuable, and their construction is well worth the expenditure of public money" (W. P. Mason, "Examination of Water," p. 29). Although the work is not far enough advanced for map construction, the figures which follow and observations thereon will be

of chemical and hygienic interest during the visit of the British Association to Bradford.

In the first place, these British normal chlorine figures are very high in comparison with the published American data. The lowest Massachusetts figure is 0.07 part of Cl per 100,000 in the area farthest removed from the Atlantic sea-border. Here the lowest found has been 0.7 part per 100,000 in the upper reaches of the Wharf, and all round it appears that the Yorkshire figures are about ten times larger than those of the State of Massachusetts, which is to be accounted for (1) by the closeness of the sea-border on either side to the Pennine range, and (2) by the density of population in, and the antiquity of, the inhabited areas.

The unit isochlor area is co-extensive with the highest hills and their becks, deans, and gills. The following chlorine determinations with waters from the upper reaches of the Wharf, Wenning, Ribble, Aire, and Calder will be sufficiently illustrative:—

		Chlorine, Parts per 100,000.
Barden	1.0	
Grimwith Beck	1.2	
Gate-up-Gill	0.7	
Bleabeck	1.0	
Buckden Pike	1.0	
Starbottom	0.8	
Kettlewell	1.0	
Buckden Village	1.2	
Gaping Ghyll	1.2	
Beck Head, Clapdale	1.3	
Ingleborough Cave	1.2	
Lower Bentham	1.4	
Malham Tarn Outlet	1.0	
Malham Cove	0.95	
Airehead	1.0	
Old Smelt Mill	1.1	
Gordale Beck	1.2	
Hanlith Bridge	1.1	
Hardcastle Craggs	1.1	
Walshaw Dean	1.1	

As the sea is approached, and more populous districts are reached, the chlorine rises, and remarkable examples of rise may be met with on the same hill slope. Halifax furnishes a striking instance. The town rests on a sloping bed of millstone grit, the ancient and most thickly populated part being towards the bottom of the incline. The ground waters of the highest parts (Mount Tabor) vary from 1.6 to 2.6; widely separated wells about half-way down yield the figure 3.8; while, towards the bottom of the slope, two wells give the figures 4.7 and 5.5. The public water supply from Pennine gathering grounds, 10 miles away, stands at 1.3.

The figures obtained for other parts of the West Riding have not yet been collated, and are therefore reserved for a further communication.

ON A LIMITING STANDARD OF ACIDITY FOR MOORLAND WATERS.*

By WILLIAM ACKROYD, F.I.C., Public Analyst for Halifax.

MANY large towns, more especially in the West Riding of Yorkshire, have their public water supplies of Moorland origin. The case of Milnes v. the Huddersfield Corporation in 1881 gave great prominence to the fact that this class of water may give rise to plumbism. No satisfactory explanation could be given at the time, and it is only during the present decade that it has been clearly understood that the plumbo-solvent action of moorland waters

* Read before the British Association (Section B), Bradford Meeting, 1900.

* Read before the British Association (Section B), Bradford Meeting, 1900.

is to be associated with acidity. An idea of the relation is furnished by the following determinations:—

Parts per 100,000.		Lead dissolved from	
Acidity in equivalent of sulphuric acid.		1-inch piping.	
1.	0.29	In 1 hour	.. 0.03
2.	0.30	" 1 "	.. 0.057
3.	0.29	" 1 "	.. 0.025
4.	1.34	" 1 "	.. 0.71
5.	1.59	" 1 "	.. 0.95

The acidity is due to carbonic anhydride and peaty acids, and the total is found by ascertaining the number of c.c. of N/100 alkali required to neutralise 100 c.c. of the water, the result being expressed as sulphuric acid. Phenolphthalein is used as the indicator.

The acidity may be very high, as from peaty gathering grounds of small incline, say 1 in 44; or comparatively low in gathering grounds of steep incline, say 1 in 12 (Ackroyd, *Journ. Chem. Soc.*, 1899, p. 199).

In the former case, violent action on lead precludes its use for domestic consumption, and in the latter even a limit must be placed on the degree of acidity allowable. During epidemics of plumbism in the West Riding, much diversity of opinion has been expressed on various points connected with the matter which the author cannot discuss here; he contents himself with stating that, after some years of experience, he has never learnt of the occurrence of any case of plumbism where the acidity of the water has been under the equivalent of 0.5 part of sulphuric acid per 100,000 of water, and this he tentatively proposes as a limiting standard of acidity for potable waters of moorland origin when the acidity is determined in the manner already described with phenolphthalein as indicator.

The average acidity of nine samples of water not above suspicion in this respect was 0.63, ranging from 0.53 to 0.91; while, on the other hand, sixty-one samples above reproach, from neighbourhoods where plumbism has not been known, had an average acidity of 0.27, the extremes being 0.20 and 0.41.

INTERACTION OF FURFURALDEHYDE AND CARO'S REAGENT.*

By C. F. CROSS, E. J. BEVAN, and J. F. BRIGGS.

In a previous paper (*Chem. Soc. Journ.*, 1899, p. 747) it was shown that hydrogen peroxide reacted with furfural to form a monohydroxy-furfuraldehyde as the main product, with simultaneous production of the corresponding carboxylic acid in small quantity. The substituting groups appear to occupy the $\alpha\beta$ positions in the ring.

The monohydroxy-furfural is identified by means of its very characteristic reactions with phloroglucinol and resorcinol, as a constituent of the lignocelluloses.

Caro's reagent, prepared from potassium persulphate and sulphuric acid according to the directions of Baeyer and Villiger (*Ber.*, 1899), reacts under similar conditions in a different manner. In the first place the reaction appears to be quantitative, and when the furfural has taken up O_2 , a trace of either reagent, in excess, persists. The temperature remaining at 15–20°, and there being no evolution of gas, we may expect to find a product of empirical formula, $C_5H_4O_4$, and as the aldehydic group disappears this should be a hydroxypyromucic acid. On reduction with sodium amalgam an aldehydic product is obtained with the brilliant colour reactions of the monohydroxyfurfurals. Control observations on pyromucic acid proved that this acid is reduced under similar conditions to furfural.

The reactions of this hydroxyfurfural, though similar to those described in our previous paper, are sufficiently differentiated to indicate that we have obtained a second isomeride. Moreover, the corresponding acids are differentiated—the one giving Pb and Ba salts insoluble in acetic acid; the salts of the new acid are soluble, and, moreover, the acid undergoes hydrolysis with such ease as to make its isolation in the pure state a matter of great difficulty. In the course of the usual processes for isolating the Ba and Ca salts, decomposition occurs, and the crystalline salts isolated are those of a dibasic acid. On boiling the original product in solution at constant volume, formic acid distils continuously and with traces only of other acids. The yield of formic acid amounted in one experiment to 0.7 grm. per 1 grm. of original furfural. All these observations indicate that the original product of oxidation is the acid $C_4H_2O_4(COOH)(OH)aa'$. A characteristic reaction of this original acid is the production of a yellowish-red precipitate with ferric chloride, similar to that obtained with pyromucic acid.

It is to be noted that the Caro reagent oxidises the constituent of the lignocelluloses which gives the brilliant colour reactions with phenols characteristic of these natural products, which we know to be a hydroxyfurfural. In this respect the reagent differs from the oxidants ordinarily used for bleaching purposes, e.g., hypochlorites and permanganates.

A quantitative experiment with a typical aldose (dextrose) and the Caro reagent, gave the somewhat unexpected entirely negative result. The cupric reduction (Fehling solution) was unaffected.

The typical ketose levulose, on the other hand, is slowly oxidised.

All of these matters are under investigation.

ON A SIMPLE AND ACCURATE METHOD FOR ESTIMATING THE DISSOLVED OXYGEN IN FRESH WATER, SEA-WATER, SEWAGE EFFLUENTS, &c.*

By Professor LETTS, D.Sc., Ph.D., &c., and R. F. BLAKE, F.I.C., F.C.S., Queen's College, Belfast.

AFTER criticising the existing methods for determining the dissolved oxygen in water volumetrically, the authors describe a very simple and accurate method for the purpose, of which the following is an outline:—

An ordinary separating funnel is filled with the water to be examined, and a measured volume withdrawn. A definite volume of standard ferrous sulphate solution is then added, and afterwards ammonia—the volume of these two reagents together corresponding with that of the water removed—and the stopper of the funnel is then inserted, care being taken that no air bubbles are enclosed.

Within the separating funnel there is now a layer of ferrous sulphate below, next the water, and above all the ammonia. These are mixed by inverting the vessel once or twice by a swinging motion, when a greenish turbid mixture results, which rapidly darkens as the dissolved oxygen is absorbed. After fifteen minutes the vessel (still stoppered) is inverted, and its tube or lower extremity (now, however, the upper one) is nearly filled with a mixture of equal volumes of sulphuric acid and water. The tap is then opened, when the acid flows downwards into the alkaline mixture, and in the course of a few minutes dissolves the iron hydrates, forming a clear solution. This is then run off into a porcelain dish, and there titrated, either with permanganate or bichromate, conveniently of the strength 1 c.c. = 1 c.c. of dissolved oxygen at N.T.P.

In the authors' experiment the separating funnel had a capacity of 332.5 c.c., practically $\frac{1}{3}$ litre; and its tube

* Read before the British Association (Section B), Bradford Meeting, 1900.

* Read before the British Association (Section B), Bradford Meeting, 1900.

Liquid analysed.	Titrations made with—	Dissolved oxygen per litre of fluid.		Difference.
		Found.	True amount.	
Distilled water saturated with air at 13°7'	Permanganate	7·26	7·20 (Roscoe and Lunt) ..	+0·06
Belfast water (town supply)	Permanganate	5·80	5·75 (Gasometric analysis)	+0·05
Sea-water from Belfast Lough	Permanganate	5·53	5·10 (Gasometric analysis)	+0·43
Sea-water from Belfast Lough	Bichromate ..	5·10		0·00
Sewage effluent from "bacteria beds" ..	Permanganate	0·66	0·36 (Gasometric analysis)	+0·30
Sewage effluent from "bacteria beds" ..	Bichromate ..	0·42		+0·06

contained, when nearly full, about 8 c.c. of diluted sulphuric acid. About 7 c.c. of the water was removed, 5 c.c. of standard ferrous sulphate solution added, and about 2 c.c. of strong ammonia. The ferrous sulphate solution contained about 12 grms. of the crystallised salt in 250 c.c. of distilled water. It was standardised for each determination by titrating 5 c.c. in a porcelain basin, mixed with the same volume of the water under examination as employed in the dissolved oxygen determination and the same volume of acid.

For all practical purposes the dissolved oxygen contained in the volume of water which the separating funnel holds amounts to the difference between the burette readings for the blank experiment and for the actual determination. The accompanying table gives a few typical results.

It will be seen that for sea-water and sewage effluents bichromate gives more accurate results than permanganate.

THE SEA-WEED *ULVA LATISSIMA* AND ITS RELATION TO THE POLLUTION OF SEA-WATER BY SEWAGE.*

By Professor LETTS, D.Sc., Ph.D., and JOHN HAWTHORN,
B.A., Queen's College, Belfast.

FOR a number of years past a very serious nuisance has arisen from the sloblands of the upper reaches of Belfast Lough during the summer months, the stench at low tide being quite overpowering, and the air heavily charged with sulphuretted hydrogen. A precisely similar nuisance, though not of the same magnitude, also arises from the sloblands in the northern portion of Dublin Bay.

The nuisance is caused by deposits of the green sea-weed, called *Ulva latissima*, or sea-lettuce, which in the two localities mentioned grows in abundance, and during high winds or gales is washed ashore. In Belfast Lough the quantity thus deposited is enormous, forming banks which are often several feet thick, and extend for miles along the coast. Once deposited, these layers of sea-weed often remain more or less stationary for months in the shallow bays or pools of the neighbourhood, and in warm weather rapid putrefaction occurs, and a perfectly intolerable stench arises, which is perceptible over a wide area, and seriously affects not only the comfort of the inhabitants of the district, but the value of their property also.

The chemical changes which occur when *Ulva latissima* ferments in sea-water.—An extended investigation in the laboratory has shown that when the sea-weed ferments, hydrogen and carbonic anhydride are first evolved in about equal proportions by volume, and fatty acids are produced. Isolation and examination of these latter show that propionic acid is the chief; butyric acid is also formed, and probably acetic acid in addition. In a later stage of the fermentation sulphides are formed, probably by reduction of sulphates present in the sea-water, and the sea-weed blackens from formation of ferrous sulphide, and this latter disengages sulphuretted hydrogen by the action of the fatty acids, whence the nuisance.

Composition of *Ulva latissima*.—The mean results of the analysis of the dried sea-weed were as follows:—

Carbon	35·15	{ Sulphur 3·21 Iron .. 2·20
Hydrogen	5·27	
Nitrogen	6·25	
Oxygen	37·96	
Ash	15·37 containing	
	100·00	

Attempts to isolate any definite principles by the methods of proximate analysis were not very successful, and no carbohydrate beyond cellulose could be identified.

Bacteriological Examination.—Considerable difficulty was experienced in attempts to isolate the organisms concerned in the putrefactive processes, and the ordinary methods failed for the greater part. The evidence at present collected points to there being two chief species concerned. (1) A spore-forming bacillus which apparently infests the sea-weed and causes the production of fatty acids from its tissues; and (2) a second micro-organism, probably derived from the mud of the shore, which gives rise to the formation of sulphides by a later fermentative process.

Ulva latissima in Relation to Sewage Pollution.—The evidence tending to prove that the occurrence of the sea-weed in quantity in any locality is associated with sewage pollution is of three kinds:—

(1). *The Composition of its Tissues*.—The amount of nitrogen it contains is far in excess of that of any other sea-weed of which analyses are recorded. It contains over 6 per cent, and resembles in nitrogen content an animal product rather than a vegetable. (Dry cheese contains about 7, and dry milk about 5 per cent, whereas peas only contain about 4 and meadow hay 2 per cent.)

(2). *Assimilation Experiments*.—A frond of the sea-weed was placed in various mixtures in succession, (a) of polluted sea-water, (b) polluted sea-water plus sewage, (c) polluted sea-water with sewage and ammonium salt, (d) sea-water plus nitrates. By determinations of free and albumenoid ammonia, and nitrates in these mixtures before and after the sea-weed had been in contact with them, the power of assimilating nitrogen which the weed possesses was ascertained and was found to be remarkably high. Thus in one experiment it absorbed the whole of the free ammonia from a polluted sea-water containing 0·050 part per 100,000 in seventeen hours. Nitrates were also rapidly absorbed, but not albumenoid matters. The weed remained in perfect health during these experiments and is still growing, although nine months have elapsed since the experiments were commenced.

(3). *The Localities where Ulva latissima abounds, and from which it is virtually absent*.—As stated above, the sea-weed is present in abundance in Belfast Lough, but it is almost entirely absent from Strangford Lough, which is similar in area and in many other respects to Belfast Lough, but differs from it in not being extensively polluted by sewage. In Dublin Bay the sea-weed is found in quantity in the harbour, which is highly polluted, but not in the southern parts of the bay, which receives no sewage, except near Kingstown, where a large sewage tank discharges on the ebb tide. There the weed occurs.

The evidence which the authors have collected tends therefore to the conclusion that the occurrence of *Ulva*

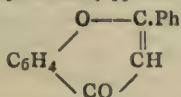
* Read before the British Association (Section B), Bradford Meeting, 1900.

Latissima in quantity in a given locality is an indication of sewage contamination, and there can be no doubt as to the power which the weed possesses of absorbing nitrogen compounds from polluted sea-water. While thus acting as scavenger it may itself give rise to a very extensive nuisance.

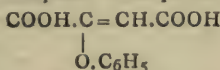
ON THE SYNTHESIS OF BENZO- γ -PYRONE.*

By Dr. S. RUHEMANN and H. E. STAPLETON, B.A. (Oxon).

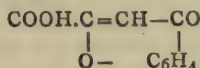
THE important group of yellow vegetable dyes, the chief of which are chrysin, fisetin, and morin, are derived primarily from a phenyl benzo- γ pyrone—



This was synthesised in 1898 by Kostanecki, but the mother substance itself, benzo- γ -pyrone, had not, up to the middle of 1900, been isolated. The authors succeeded in preparing this compound from phenoxy-fumaric acid—



This acid dissolves with evolution of heat in concentrated sulphuric acid, and on diluting the solution with water a new acid is precipitated which was found to be benzo- γ -pyrone carboxylic acid—



On distillation *in vacuo* this broke up with the evolution of carbon dioxide, and a liquid distilled over which slowly solidified. It crystallised from a mixture of benzene and ligroin in flat needles which melted at 59°. and analysis showed it to be benzo- γ -pyrone. The yellowish solution of benzo- γ -pyrone in concentrated sulphuric acid possesses a violet fluorescence.

A SIMPLE METHOD FOR COMPARING THE "AFFINITIES" OF CERTAIN ACIDS.*

By HENRY J. HORSTMAN FENTON, F.R.S.,
and
HUMPHREY OWEN JONES, B.A., B.Sc.

In a former communication (*Trans. Chem. Soc.*, lxxvii., 1900), the authors have described the isolation and properties of free oxalacetic acid, and several interesting reactions of this acid are now being investigated. During a more extended study of the *hydrazone* the following somewhat remarkable behaviour has been observed. Heated with dilute sulphuric acid it is transformed, as was previously shown (*Trans. Chem. Soc.*, lxxvii., 1900), into Wislicenus's phenylpyrazolon carboxylic acid—



but in order that this change may be complete it is now found that a certain minimum concentration of the acid is necessary. When heated with pure water an entirely different result is obtained: carbon dioxide is evolved, and the *hydrazone* of pyruvic acid separates in the crystalline state— $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_4 = \text{C}_9\text{H}_{10}\text{N}_2\text{O}_2 + \text{CO}_2$. If the concentration of the acid falls below this necessary minimum both reactions occur simultaneously, even though the acid is present in excess; with decinormal sulphuric acid, for example, about 26 per cent undergoes the second change

A preliminary set of observations has been made with the following acids, using decinormal solutions and measuring the evolved carbon dioxide in a specially constructed apparatus—hydrochloric, nitric, sulphuric, trichloroacetic, tartaric, malic, succinic, citric, acetic. The results obtained indicate that the amounts of carbon dioxide evolved are in the inverse order of the concentration of the hydrogen ions, so that a comparison can be made of the relative "strengths" or "affinities" of the acids. The order obtained with the above acids agrees remarkably well with that resulting from the other well-established methods.

DERIVATIVES OF METHYL-FURFURAL.*

By HENRY J. HORSTMAN FENTON, F.R.S.,
and
Miss MILDRED GOSTLING, B.Sc.

THE authors have previously shown that an intense purple colour results when *lævulose*, cane sugar, sorbose, or inulin is acted upon by dry hydrogen bromide in ethereal solution. The colour-giving substance was isolated in a crystalline state and was shown to be *bromo-methyl-furfural*, its formation being characteristic of ketohexoses, or substances which yield them on hydrolysis. This substance is now the subject of further investigation, and the following results have so far been obtained:—

When acted upon by stannous chloride in acid solution the bromine is easily replaced by hydrogen, and the resulting liquid is identical in every way with δ -methyl-furfural; so that the reaction affords by far the simplest method for the preparation of the latter substance in a pure state.

The bromo-compound, when dissolved in appropriate solvents, readily reacts with various silver salts, giving rise often to beautifully crystalline compounds; the acetoxy- and benzoxy-derivatives have, for example, been prepared and analysed. By the action of sulphurous acid, these, like the parent compound, yield the remarkable condensation product $\text{C}_{11}\text{H}_8\text{O}_4$, which gives beautiful colour-reactions with caustic alkalis and with aniline. This condensation-product has also been further studied, and the results so far favour the author's original suggestion that it is a dicarbonyl compound.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, September 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

* Read before the British Association (Section B), Bradford Meeting, 1900

* Read before the British Association (Section B), Bradford Meeting, 1900.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month has been considerably more than it was in July; 3.13 inches have fallen, the average being 2.32 inches; we have therefore to record an excess of 0.81 inch of rain for the month. This reduces the previous deficit for the year to 0.03 inch, or 0.18 per cent on the thirty years' average.

Our bacteriological examinations of 544 samples have given the results recorded in the following table; we have also examined 39 other samples, from special standpipes, &c., making a total of 583 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	94
New River, filtered (mean of 130 samples) ..	4
Thames, unfiltered (mean of 26 samples) ..	2349
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 297 samples) ..	9
Ditto ditto highest	106
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	138
River Lea, from the East London Company's clear-water wells (mean of 39 samples) ..	8

Of the 466 samples of filtered water supplied to London, examined bacteriologically during the last month, only one sample contained over 100 microbes per c.c. This shows that the usual efficient filtration has been more than maintained.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

ON THE TRANSMUTATION OF PHOSPHORUS INTO ARSENIC AND ANTIMONY.

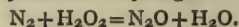
By F. FITTICA.

I MUST beg to be allowed to make a few remarks on the communication made by M. Winkler (see *CHEM. NEWS*, lxxxi., p. 304), who contests the possibility of the transmutation of phosphorus into arsenic. It is more or less true that the experiments I made at the Chemical Institute at Marbourg have a slightly alchemistic appearance, but unfortunately I must confess that, even at the present day, I maintain the opinion I defended many years ago. At the time to which I refer, I said, at a conference at which I was present, "At heart we are still alchemists, not actually in the sense of making gold, but from the point of view of the possibility of transmuting metals. If it is true, and we have a right to suppose it so, that the metals as we know them are not elements, if it is true that there is only one element, as suggested by v. Helmont, or that there are even four, as imagined by the ancients, we ought to succeed, in the more or less near future, in transmuting the elements, and thus solving the old problem of alchemy." I made the above statement about twelve years ago. I also added that we had no need of the philosopher's stone for effecting the transmutation of metals. Since that time I have become more and more persuaded that the simplest thing is the most perfect, that nature has recourse to the most simple means, that the force of affinity combining atom to atom and molecule to molecule only requires certain elements

for its manifestation. What fault can be found in that? Is it not, on the contrary, the duty of the chemist and the naturalist to study the harmony of the universe, to show that the marvels of nature are accomplished by the aid of means, forces, and materials of the most simple kind, instead of accumulating, according to a given scheme, compound on compound forming even at the present time an almost inextricable tangle? It stands to reason that this study must be based on exact experimental methods.

Has M. Winkler proved that my methods are inexact or false? In no way. Although he claims to have rigorously followed my instructions for the principal reaction, he has in reality modified it, after finding that it was rather difficult to carry out. Now it is necessary to take the trouble to make an intimate mixture of red phosphorus and nitrate of ammonium, and it is also necessary to apply the heat very carefully to reach the temperature given, 180°. But by following M. Winkler's method, that is to say, by throwing the amorphous phosphorus into the fused nitrate of ammonium, a modification of the highest importance is at once made, as it has long been known that phosphorus burns in an atmosphere of protoxide of nitrogen (fused nitrate of ammonium) as readily as in a current of pure oxygen. On the other hand, the experiments of Spring (*Jahresbericht der Chemie*, 1888, 67; *Arch. Pharm.*, 1892, 230, 159) prove that, pressure alone suffices to combine these bodies when very intimately mixed, and, further, that it is by no means unimportant whether these bodies should be mixed in coarse particles or in a finely divided state using the greatest care. Now, M. Winkler simply produced the combustion of phosphorus in protoxide of nitrogen.

He has not checked the other methods I described, and which enabled me to prove the following facts. On heating amorphous phosphorus with peroxide of barium and dilute nitric acid, we get complete oxidation without the least trace of arsenic being formed; by replacing the dilute nitric acid by strong acid, and operating in the presence of peroxide of barium more or less strong, traces of arsenic are formed. But instead of using strong nitric acid, M. Winkler used chlorine. Further, by causing an energetic oxidising agent, such as sodic hydrate or peroxide of hydrogen, to act on amorphous phosphorus, we are right in supposing that the nitrogen of the air intervenes in the formation of arsenic. In the same manner as ordinary phosphorus sets free the nitrogen of the air, amorphous phosphorus liberates it in the presence of sodic hydrate, and the following reaction takes place in the presence of peroxide of hydrogen:—



This conclusion is so much the less a gratuitous assertion as we do not forget that even the easily decomposed nitrogen compounds, such as ammonia, form arsenic in a similar manner with the help of ordinary phosphorus. We also know that in a strongly alkaline solution the nitrogen of the air undergoes a series of transformations, and in this respect even M. Winkler himself has observed the decomposition of protoxide of nitrogen by amorphous phosphorus.

I will now describe some fresh experiments which have shown the possibility of transmuting phosphorus into antimony. These experiments are not yet completely finished, and I shall have more to say on the subject later on, but for the present they warrant me in stating that antimony is also a nitrated compound of phosphorus. Even at the commencement of my experiments with arsenic I sometimes noticed the formation of a small quantity of antimony as well as arsenic, when nitrite of potassium was used as well as nitrate of ammonium, and the temperature was somewhat increased. I therefore made a series of experiments with a view to making sure of the transmutation of phosphorus into antimony, either alone or mixed with arsenic. I soon found, however, that there were innumerable difficulties to be overcome. By placing ordinary phosphorus in contact with nitrite of potassium

and nitrate of ammonium, phosphoric acid alone is formed. A mixture of amorphous phosphorus, nitrate of ammonium, nitrite of potassium, and potassic hydrate, gives rise to a very vigorous reaction, but the yield is so uncertain that sometimes only arsenic is obtained. The same is the case when we replace the hydrate by carbonate of potassium. When, on the other hand, we substitute peroxide of barium for the nitrite of potassium, we obtain a mass which explodes on heating, especially if no potash is present. A mixture of amorphous phosphorus, nitrite of ammonium and saltpetre, also gives rise to an explosive body. By throwing the latter into fused potash, the reaction is less lively though accompanied by luminous phenomena, but in this case also the result is so uncertain that frequently only arsenic is obtained.

An intimate mixture of amorphous phosphorus, nitrite of potassium, and nitrate of ammonium, without the addition of hydrate or carbonate of potassium, bursts into flame instantly, and practically nothing but phosphoric acid is formed. It is for this reason that carbonate of ammonium has been added to this last mixture, when certainly an action took place,—that is to say, a lively reaction occurred at a temperature below the boiling-point of water, but this temperature did not seem to be sufficient to make the change complete. On then heating over a naked flame a vigorous reaction again occurred, but at a temperature above 100° a violent explosion soon took place. To guard against this danger I did the heating on a sand-bath, in a tube traversed by a current of carbonic anhydride and connected to a condenser, and I found that a mixture of amorphous phosphorus, nitrate of ammonium, nitrite of potassium, and carbonate of ammonium, commenced to react at 70° to 75° , and that the reaction became very lively between 90° and 100° . At this point it became calmer, and continued in a tranquil manner to a temperature above 145° , reaching its end at 150° to 155° , with the accompaniment of luminous phenomena or even of explosion. The mass formed at 140° to 145° consists of a brown compound insoluble in water. It contains antimony in quantities easy to detect, as well as phosphorus, and seems to be phosphoretted antimony (*Fahresbericht der Chemie*, 1873, 229). It is probably this latter body that causes the violent decomposition at a slightly elevated temperature. The antimony does not appear to be accompanied by arsenic at the above-mentioned temperature, but in any case this body only occurs in traces.—*Chemiker Zeitung*, 1900, p. 561.

the intervention of cuprous chloride is made use of. 4. Pan processes; and 5. Barrel processes, which are, however, almost obsolete.

The object of Lixiviation processes, dealt with in Section III., is to extract the silver in the form of a solution, from which it can be afterwards precipitated by appropriate means. There are practically only two salts of silver which can be used for these processes, the chloride and the sulphate; the former may be dissolved out by brine or decomposed by sodium hyposulphite, with which silver forms a series of soluble double salts, while the sulphate simply requires hot water for its solution. There are three main series of lixiviation processes in which the above characteristics of silver salts are made use of; they are known as the Augustin, Ziervogel, and Patara processes.

The use of ammonia for dissolving silver chloride was actually tried at the Broken Hill mine, but the loss of ammonia was much too great, besides being most inconvenient in other ways.

The smelting of silver ores, to which Section IV. is devoted, together with enough lead-bearing material to carry away the whole of the silver, is practically identical with the blast-furnace smelting of lead ores; but in the absence of lead, matte or speiss may be relied upon to effect a perfect collection of the precious metals. The use of matte has recently undergone remarkable extension through the introduction of practical means for utilising the sulphur in the ore as a source of heat in the modern system called pyretic smelting, and it has the further advantage of permitting a higher degree of concentration without undue loss.

Looked at from the practical point of view, this work has fully achieved its object; the author has produced a first-class book for practical men, and, aided by the masterly editorship of Sir W. C. Roberts-Austen, has collated and arranged his sections and details so as to combine the maximum of information with the minimum of repetition.

The text is adorned with a number of useful illustrations, and is furnished with a copious Index of over fifteen pages, but we are sorry to see a rather long list of errata.

NOTICES OF BOOKS.

The Metallurgy of Lead and Silver. By HENRY F. COLLINS, A.R.S.M., A.M.I.C.E., &c. Part II., Silver. Edited by Sir W. C. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S. With numerous Illustrations. London: Charles Griffin and Co., Ltd. 1900. Pp. 352.

As in Part I., on Lead, obsolete processes have received only casual consideration, the aim throughout being to consider the subject from the practical standpoint of the working metallurgist.

The book is divided into four principal sections: on Silver and its Ores; Amalgamation processes; Lixiviation processes; and Smelting processes. The first Section deals only with the properties of silver and its principal compounds, and enumerates the principal ores of silver.

Section II. is the largest, as all silver ores, however complex, can be treated by amalgamation after a preliminary roasting with salt; but this, while adding to the expense, also causes additional loss by volatilisation, and in most cases, unless the ore can be amalgamated direct, it is better to adopt a lixiviation or smelting process. Amalgamation processes can be divided under five heads: 1. Direct amalgamation. 2. The Mexican or Patio process. 3. The Cazo, Fondon, or Tina processes, in which

The Scientific Foundations of Analytical Chemistry Treated in an Elementary Manner. By WILHELM OSTWALD, Ph.D., Professor of Chemistry in the University of Leipzig. Translated, with the Author's sanction, by GEORGE MCGOWAN, Ph.D. Second English Edition, translated from the Second German Edition, with further alterations and additions by the Author. London: Macmillan and Co., Ltd. New York: The Macmillan Co. 1900.

ENCOURAGED by the reception of the first edition, which, within three years, has been translated into English, Russian, Hungarian, and Japanese, the author has brought out a second edition, for an English translation of which we are again indebted to Prof. McGowan. The present work is thoroughly revised, and contains many additions. The author says he has "withstood the inclination to enter into greater detail than formerly, in the second part of the book." This is much to be regretted, for the principles involved are of such magnitude and the reasoning so sound that a little more elaboration would be welcome.

We can strongly recommend the book both to advanced chemists and to analytical students, for there is a notorious want of attention to foundation truths in most of the present systems of chemical study, and it is the author's knowledge of this want that called forth the present volume. There is one paragraph in the preface that is so characteristic that we must quote it as giving the key to the whole book:—

"That there is no such thing as a perfectly insoluble substance, and that absolutely exact methods of separation and estimation are an impossibility—remain not merely

unknown to the student, but also occur less frequently, I fear, to the mind of the accomplished analyst than is to be desired in the interests of a sound criticism of analytical methods and their results."

The peculiar charm of Prof. Ostwald's writing is in no way lost in the translation, and a study of the volume will help the student to clearly and pleasurably grasp the principles of the science.

Acetylene. A Handbook for the Student and Manufacturer. By VIVIAN B. LEWES, F.I.C., &c., Professor of Chemistry, Royal Naval College, Greenwich; Chief Superintending Gas Examiner to the Corporation of the City of London, &c. Westminster: Archibald Constable and Co., Ltd. New York: The Macmillan Company. 1900.

CHAPTER I., Part I., gives a clear and comprehensive history of acetylene, from its discovery by Edmund Davy, in 1836, to its commercial production in 1895. The remainder of Part I. is taken up with descriptions of the preparation, properties, and chemical reactions of the gas, recounting much of the detailed communications of those who have recently worked upon the subject. The question of priority of the discovery of the commercial production of calcium carbide is given at length, and includes letters between Mr. Thomas L. Willson and Lord Kelvin upon the subject.

Part II. commences with the Electric Furnace, and gives a complete account of the present manufacture, properties, and impurities of calcium carbide, and the production of acetylene.

Part III. contains the legal enactments in force in various countries, and extracts of English patents for generators and burners, &c.

The whole subject is dealt with in great detail, the book comprising nearly a thousand pages with over two hundred illustrations. There is also an appendix with weights and measures, tables of atomic weights, &c., which seem a little out of place. The book will be of great service to all interested in the manufacture and commercial uses of acetylene.

Les Nouveautés Chimiques pour 1900 (Chemical Novelties for 1900). By M. CAMILLE POULENC. With 182 Figures in the Text. Paris: J. B. Baillière et Fils. 1900. Pp. 292.

This volume will be of great service to chemists, inasmuch that it contains an account of the latest new methods and apparatus introduced for use in commercial chemistry and scientific research.

In the first chapter we find chiefly apparatus designed for the determination of densities, temperatures, solubilities, &c.

The second chapter is principally concerned with apparatus for facilitating and simplifying long and tedious manipulations; it also contains an account of several new types of gas-burners, a new form of mercury pump in which the mercury is raised automatically, designed by M. Berlemont, an apparatus for the manufacture of acetylene black, &c.

The third chapter comprises electrical apparatus of all kinds, including a new electric furnace by Dr. Helbig, some new forms of interruptors, &c.

The fourth chapter deals with general analytical chemistry: among the novelties in this subject will be found a very ingenious apparatus introduced by M. le Docte, for gas analysis, by means of which the operations are much simplified; there is also to be found a new colorimetric method for the estimation of nitrogen.

Finally, in chapter five, we find the latest improvements in bacteriological methods and apparatus, among which may be mentioned Lequeux's electric sterilising oven.

CORRESPONDENCE.

THE SOCIETY OF CHEMICAL INDUSTRY OF VICTORIA.

To the Editor of the Chemical News.

SIR,—I am instructed by the Council to send you notice of the formation of the above Society.

Enclosed you will find a copy of the circular issued by the Provisional Committee, to which I have made some additions.

The number of members enrolled so far is 118.

The first paper is to be read on September 4th, 1900, by Dr. Avery, M.Sc., on "The Cyanide Process for Gold Extraction."—I am, &c.,

HERBERT W. GEPP, Hon. Sec.

Australian Explosives and Chemical Co.,
Deerpark, Victoria, Australia,
August 27, 1900.

(CIRCULAR).

At a meeting held on the 12th of June at the University, at which between thirty and forty gentlemen representing Chemical and Allied Industries were present, it was unanimously resolved to form a Society to be called "The Society of Chemical Industry of Victoria."

The objects for which the Society is established are:—

- To afford its members opportunities of meeting, and discussing matters connected with Applied and Industrial Chemistry.
- Generally to advance the cause of Chemical Industry in Victoria.

The Society will be open to all who are interested in Industrial Chemistry.

It is proposed that the work of the Society shall be carried on by the following means:—

A meeting will be held once a month during the greater part of the year, at which papers will be read and discussed on some special branch of Industrial Chemistry.

Such meetings will enable members to become personally known to one another, and will encourage the interchange of knowledge and opinions.

Special Committees may be appointed from time to time to report upon questions of interest to those engaged in the Manufacture or Sale of Chemicals, such as want of uniformity in analytical methods or laws affecting Chemical Industries.

Occasionally it may be found advisable to print, for issue to members of the Society, papers that have been read at its meetings, reports of Special Committees, or other matter of general interest. But it is not proposed, at present at all events, to attempt the publication of a journal.

The very great success of the English Society of Chemical Industry, which was established in 1882, and now has over two thousand members on its roll, affords striking proof of the good to be done by such an Association. Much of the work of that Society is done by the meetings of its various local sections, and there can be little doubt that what has proved so great a boon to Chemists in London, Liverpool, Manchester, Nottingham, Glasgow, and other industrial centres at home, will succeed in Melbourne also.

It is indeed certain that the want of such an organisation has been felt in the past, and it is time that this want were met.

I am instructed by the Provisional Committee to invite you to become one of the Original Members of the Society. If you desire to do so, will you kindly fill in and return the enclosed form as soon as you conveniently can.

Notice will then be sent you of the first General Meeting, together with a copy of the laws as drafted by the Provisional Committee. The business of the General

Meeting will include the adoption of the Laws of the Society and the election of office-bearers.

The first annual subscription, which has been fixed at 10s. 6d., may be paid to me at or before that meeting.

HERBERT W. GEPP,
Hon. Secretary of the Provisional Committee.

Provisional Committee :—

Professor ORME MASSON, the University of Melbourne (Chairman), elected President.

D. AVERY, Lecturer on Chemistry at the Working Men's College, elected Hon. Treasurer.

J. KERR FORREST, care of Messrs. Felton, Grimwade, and Co.

C. NAPIER HAKE, Chief Inspector of Explosives, elected Vice-President.

WM. KITCHEN, care of J. Kitchen and Sons, South Melbourne, elected Vice-President.

W. A. MILLER, care of Colonial Sugar Refining Co., Yarraville.

A. PARKER, Metallurgical Works, Footscray.

F. STEEL, care of Cuming, Smith and Co., Yarraville.

H. W. GEPP, care of Australian Explosives Co., Ltd. (Hon. Sec.).

The Council elected at the First General Meeting consists of the above, with the following additions :—

JAMES CUMING, jun., care of Cuming, Smith, and Co., to be a Vice-President.

A. N. PEARSON, Chemist to the Departments of Agriculture, Water Supply, &c., of Victoria.

HENRY C. JENKINS, Victorian Government Metallurgist.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

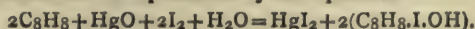
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 11, September 10, 1900.

Nitrocelluloses.—Léo Vignon.—This paper contains an account of a series of experiments on the reducing power of the nitrogen derivatives of cellulose, and on the creation of these reducing powers by nitration. Two specimens of nitrocellulose and of nitro-oxycellulose were prepared. In the first experiment of each series the nitration was allowed to attain its maximum, in the second a lower nitrated product was obtained. The same operations were performed when oxycellulose (prepared by means of chlorate of potash and hydrochloric acid) was substituted for cellulose. Four products were obtained, in which the author estimates the nitrogen present as a measure of the degree of nitration. He concludes from the numbers deduced—(1) That nitrated celluloses and oxycelluloses energetically reduce cupro-potassic solutions; (2) that their reducing power is independent of the degree of nitration of cellulose or of oxycellulose; (3) the reducing power is almost the same for nitrated cellulose and for nitrated oxycellulose; (4) finally, that the reducing power sensibly constant with regard to nitrocellulose or nitro-oxycellulose, is about one-fifth of that of "invert sugar."

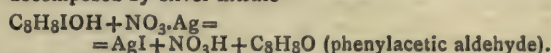
No. 12, September 17, 1900.

Decomposition of Nitric Ethers and Nitroglycerin by Alkalis, and the Relative Stability of Explosive Materials.—M. Berthelot.—In general, ethers are decomposed by alkaline hydrates with formation of the acid and alcohol corresponding to the ether. However, nitric ethers offer certain exceptions to this rule. The author observed that nitric ethers treated with concentrated alkaline solutions can produce methylic and ethylic ethers instead of the corresponding alcohols.

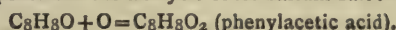
Action of Iodine and Yellow Oxide of Mercury on (1) Styrolene and 2) Safröl.—J. Bougault.—As a continuation of a former research on the action of iodine and yellow mercuric oxide on anethol, isosafrol, &c., the author studies the action of the same reagents on similar compounds, such as styrolene and safröl. The separate reactions obtained when the above substances act on styrolene can be represented by the equations—



The substance thus obtained ($\text{C}_8\text{H}_8\text{I.OH}$) is very easily decomposed by silver nitrate—



This aldehyde, when treated with alkaline silver oxide, gives phenylacetic acid, which can be recognised by its fusing-point and the analysis of its barium salt :—



The reactions are conducted in exactly the same manner with safröl. A compound being obtained by the action of I and of HgO which is an addition product of hypiodous acid; but this body, decomposed by silver nitrate, gives a substance showing none of the characteristic reactions of aldehydes. The author proposes to further investigate this compound.

Reduction of Nitrocelluloses.—Léo Vignon.—This paper is a continuation of that given in *Comptes Rendus*, cxxi., No. 11, and deals more generally with the reduction of nitrocelluloses. The author first considers the action of ferrous chloride in eliminating the NO_3 groups, but leaving intact the aldehydic groups. The reducing action of ammonium sulphide is more complicated than that of ferrous chloride; it eliminates the NO_3 groups and destroys the aldehydic group CHO. Generally it may be stated that nitrated celluloses reduced by FeCl_2 are transformed into oxycelluloses. Nitrated celluloses, treated with ammonium sulphide, give cellulose or hydrocellulose possessing no reducing power. This difference of action can be explained if we consider that, in the first case, the reduction is effected in an acid medium, and so gives the products of an oxidising reaction ($\text{Fe}_2\text{Cl}_6\text{NO}_2$), whilst, when ammonium sulphide is used, the reaction takes place in an alkaline medium; the products of the reaction, $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , being deprived of their oxidising properties. These results confirm the conclusions previously established, that nitrated celluloses ought to be considered as derivatives of oxycellulose.

Journal de Pharmacie et de Chimie,
Series 6, Vol. xii., No. 1.

Action of Wood Charcoal on the Organic Matter in Water.—F. Malméjac.—Already inserted in full.

Gasometric Estimation of Nitrites in the presence of Nitrates or other Soluble Salts.—J. Gailhat.—Already inserted in full.

Contribution to the Analysis of Sugar Materials.—G. Halphen.—The substance is placed in a flask having the 300 c.c. mark on its neck; such a quantity is taken as will represent about 30 grms. of the total sugars; water is added, and the whole shaken up with an excess of carbonate of lime to saturate the free acids; after ten minutes, neutral acetate of lead is poured into this liquid as long as a precipitate is formed, and 3 or 4 c.c. in excess added. Make up to 300 c.c., shake well, and filter. One portion of this liquid serves for the direct estimation of the reducing sugars; another is examined in the polarimeter; a third is inverted; a fourth, carefully measured (50 c.c.), is evaporated until its volume is only 5 c.c.; it is then carefully heated until dry, heated to 40° , and 0.5 c.c. of pure hydrochloric acid added; after stirring it is precipitated with alcohol. After one to two hours the clear liquid is decanted, and the residue washed with alcohol as

described by M. Raczkowski. Under these conditions the polarimetric estimation can be carried out with great accuracy.

No. 2.

Some Compounds of Diantipyrine-methane (Formopyrine).—G. Patein.—The author took 10 grms. of iodine and 10 grms. of formopyrine and dissolved each of them in 150 to 200 c.c. of alcohol at 95°; the former solution was then poured drop by drop into the latter with constant stirring; fine needles are soon formed, and these increase with each addition of iodine. These crystals have all the appearance of iodine, but they remain stable at a high temperature and do not colour starch paper, they do not melt or give off iodine until a temperature of 135° is reached. Analysis shows this compound to be a tetraiodide of formopyrine. Formopyrine also acts on pyrocatechin, forming a crystalline body corresponding to 4 molecules of pyrocatechin-monosulphonic acid to 5 grms. of formopyrine. Similar bodies are also formed by the action of formopyrine on hydroquinone, and on resorcin.

The use of Dried Pulverised Fibrine for the Estimation of Pepsin.—P. Macquaire.—The author finds that fibrine washed and dried at 40° may be advantageously substituted for fresh fibrine in the ratio of 25 grms. of dry fibrine for 100 grms. of fresh. It permits the use of a 100 c.c. flask and other convenient modifications.

MISCELLANEOUS.

Schools of Chemistry.—The following additional information of interest to Students has been received:—

SURGEONS' HALL, EDINBURGH.—Dr. Stevenson Macadam.—The courses of instruction in Chemistry, Theoretical and Technical, qualify for Graduation in Medicine and in Science in the University of Edinburgh, the University of London, and other Universities, and all other Medical and Public Boards. The Lectures on Chemistry are delivered at 10 a.m. daily during the Winter Session, in the Lecture Room, Surgeons' Hall, Nicolson Street. These Lectures form a complete course, and include Tutorial and Class Examinations. The Lectures on Practical Chemistry are delivered daily during the Winter, Spring, and Summer Sessions. The substances selected for examination and testing are those with which Medical and Pharmaceutical students are personally called upon to exhibit a practical acquaintance. Instructions in Laboratory Work as required for Science (Public Health) Degrees are conducted daily, and include the Testing of Complex Substances, the Detection of Poisons in Organic Mixtures, the Analyses of Air and other Gases, Waters, Foods, and Drugs, &c. The course of study in Technical Analytical Chemistry is arranged for instruction in ordinary Chemical Analyses bearing upon Agriculture, Mining, and Manufacturing Industries, and the prosecution of researches in Manipulative and Technical Chemistry.

Messrs. John J. Griffin and Sons, Ltd., are now introducing a lot of new apparatus for volumetric work. The graduations on the various burettes, pipettes, &c., are made with regard to the fact that 1 kilogram. of water at 15° (the ordinary temperature) is not exactly a litre, but is known as a *Mohr's litre*. The standard litre, as is well known, weighs 1 kilogram. at 4°, and is the basis on which all measuring instruments used by the German Customs' Authorities are graduated. Seeing that at 15° there is a difference of about 2 grms. between the litres of the two systems, it is of the utmost importance, if accuracy in volumetric work be desired, to know on which system the measuring instruments are graduated, and as instruments of both kinds have come into the market it has become imperative to adopt distinctive markings for the two systems. In future all instruments sold by Messrs.

Griffin and Sons on Mohr's system will be marked $\frac{\text{gram.}}{15^\circ \text{C.}}$, or $\frac{\text{grammes}}{15^\circ \text{C.}}$, while those adjusted according to the standard litre will be marked $\frac{\text{ccm.}}{15^\circ \text{C.}}$. These

latter vessels hold a standard litre or a cubic decimetre—but not a kilogramme—of water at 15°. At this temperature, and under a pressure of 760 m.m., it weighs only 998.07 grms.; a Mohr's litre under the same conditions weighs 1000 grms.

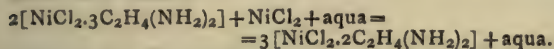
Volumeic Estimation of Nickel.—G. Giorgis.—The salts of this metal are totally precipitated in neutral solution by a solution of oxalate of barium or strontium, acidulated with oxalic acid. The precipitate has the formula $\text{C}_2\text{O}_4\text{Ni}$. We can either estimate the oxalic acid contained in the washed precipitate colorimetrically with SO_4H_2 , or estimate the oxalic acid in the excess of oxalate used in the filtered solution. Oxalate of magnesium precipitates a mixed oxalate of nickel and magnesium. The ammoniacal salts ought to be eliminated, as they interfere with the total precipitation of the oxalate.—*Gazz. Chim. Ital.* (1), vol. xxix., p. 72.

Contribution to the Study of Ruthenium and its Compounds.—V. Antony and A. Lucchesi.—The authors draw attention to the fact that no ruthenic compounds of the type RuX_4 are known which do not contain a NO group besides the halogens. They have also examined the blue compounds which are formed by the different ruthenic compounds, and have not yet been isolated. Their experiments have been carried out on the chlororuthenates and sulphate of ruthenium submitted to the action of H_2S and SO_2 . These observations are still incomplete, but full details of what has been done will be found in the original paper.—*Gazz. Chim. Ital.* (1), vol. xxix., p. 312.

The Oxidation of Camphene.—I. L. Maievsky.—On treating a solution of 30 grms. of camphene in 200 grms. of acetic acid, with a 6 per cent solution of permanganate of potash at the ordinary temperature, camphenylone, $\text{C}_{10}\text{H}_{14}\text{O}$, was obtained, giving an oxime fusible at 104.5° to 105°; the same ketone was found in the products of oxidation of camphene by nitric acid of 1.4 density diluted with its own volume of water, the mixture being heated on the water-bath for eight hours. The oxidation of camphene by CrO_3 in the presence of acetic acid, on the contrary, gives camphor, the oxime of which melts at 114°–114.5°; to effect this change a solution of 30 grms. of camphene in 150 grms. of acetic acid is added to a solution of 60 grms. of CrO_3 in 60 grms. of water and 400 grms. of acetic acid; as the reaction gives off heat the mixture is kept cool at first, and finally heated for a few instants on the water-bath. The author has also found that the aldehyde formed by the dehydration of campheneglycol becomes oxidised when shaken up with the chromic mixture at about 70° to 80°, into an acid, $\text{C}_{10}\text{H}_{16}\text{O}_2$, fusible at 54° to 58.5°, and volatile in steam.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 678.

The Ethylenediamine Compounds of Nickel.—N. S. Koursanof.—When we gradually add ethylenediamine to an aqueous solution of NiCl_2 , the colour passes from green to blue, then to reddish-violet. The blue and violet solutions may be diluted with water without changing the tint; they are distinguished by their reactions as well as by their colours, and they contain complex compounds, such as $\text{NiCl}_2 \cdot n\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot m\text{H}_2\text{O}$. On evaporation the violet solution gives violet, rhomboidal flakes, one c.m. in length, having the composition $\text{NiCl}_2 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ stable in the air. The concentrated aqueous solutions of this body are violet, the dilute solutions are a reddish-violet; their reactions indicate the existence of a radical $\text{NiCl}_2 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2$. With PtCl_4K_2 , they immediately give an abundant pale-rose precipitate, formed of microscopic needles, having the composition $\text{NiCl}_2 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{PtCl}_2$. With H_2PtCl_6 we obtain a

yellowish-brown flocculent precipitate formed of microscopic needles. Dithionate of soda gives a crystalline precipitate of the composition $\text{NiS}_2\text{O}_3 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2$. A solution of iodine in potassic iodide gives a red precipitate of the polyiodide. The addition of alcohol precipitates the violet salt from its aqueous solutions. The blue solution behaves differently; it has not been obtained in the crystalline form; when evaporated on the water-bath, or in an exsiccator, it leaves an amorphous, viscous mass of a blue colour. Its reactions indicate the presence of a radical $\text{NiCl}_2 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$, corresponding to the $\text{NiX}_{2-4}\text{NH}_3$ type of ammoniacal compounds. K_2PtCl_4 gives a precipitate $\text{NiCl}_2 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{PtCl}_2$ with the blue solution, formed of small hexagonal prisms of an orange-yellow colour. With the concentrated solution, PtCl_2Na_2 produces a yellowish-orange precipitate, formed of small quadrangular flakes, having the composition $\text{PtCl}_4 \cdot \text{NiCl}_2 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$. Alcohol and dithionate of soda do not precipitate the blue solutions; the solution of iodine in potassic iodide gives a steel-grey polyiodide. Both the solutions are decomposed by the mineral acids, and by $\text{SO}_4(\text{NH}_4)_2$. Strengthening the tint by the addition of ethylenediamine results in the successive formation of the complex compounds $\text{NiCl}_2 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$ and $\text{NiCl}_2 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2$. Reciprocally, the addition of NiCl_2 to the violet solution brings the colour back to blue by the inverse reaction—



—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 688.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Calcium Carbide.—Can any correspondent inform me under what patents, if any, calcium carbide is now manufactured?—B.

Sulphuric Acid Plant.—Calcium Phosphate.—Can any correspondent kindly inform me through the medium of your paper where any pamphlets or small books on the erecting of sulphuric acid plant can be obtained? A very small plant is required. It is for erecting in India, and I believe such small plants can be put up as would cost only about £1500. Are there any so small in existence? Further, I should be obliged for the information as to what amount of iron would be considered harmful in material showing 58 per cent tribasic phosphate of lime. Any iron is, I believe, harmful, but what is the amount which would spoil it for agricultural use? The boilers frequently become eaten by nitric acid; would treating the water before use with ferrous sulphate be advantageous?—PHOSPHATE.

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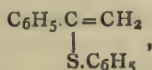
VOL. LXXXII., No. 2133.

ON THE COMBINATION OF THIOPHENOL AND GUAIACOL WITH THE ESTERS OF THE ACIDS OF THE ACETYLENE SERIES.*

By Dr. S. RUHEMANN and H. E. STAPLETON, B.A. (Oxon.).

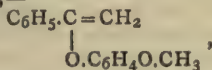
In this paper an account is given of the continuation of previous work on the combination of phenols with the esters of the acetylene acids. The authors were induced to study the action of thiophenol on these esters in the hope of finding a new method of preparing thioacetophenone, whilst the investigation of guaiacol was taken up, as no derivative of a dihydric phenol had previously been worked with.

During the progress of the research various new derivatives of thiophenylcinnamic, fumaric, and succinic acids were discovered, but it was found that thiophenyl styrene,—



on boiling with dilute mineral acids is decomposed into acetophenone and thiophenol, and not into thioacetophenone and phenol, as had been expected.

Guaiacol was found to combine readily with phenyl propiolic ester; guaiacolyl cinnamic acid and its ester were prepared, and it was found that the acid on heating quantitatively decomposed into carbon dioxide and guaiacolyl styrene,—



From the latter mineral acids regenerated guaiacol, with the additional formation of acetophenone.

HEATING AND LIGHTING POWER OF COAL-GAS.*

By T. FAIRLEY, F.R.S.E., F.I.C.

THE consumption of coal-gas for heating and gas-engine purposes is constantly increasing, and in populous districts varies from 20 to 50 per cent of the amount manufactured.

Legislation provides a candle unit for measuring the lighting power of gas, but no notice has been taken of variations in heating power.

As to the relations of heating and lighting power, opinions differ. On one side it is said that a high lighting-power gas is no better than a lower gas for heating and engine purposes (*Encycl. Brit.*, vol. x., p. 102). On the other, a definite relation has been traced between the two (Aguillon, *Comptes Rend.*, cvii., p. 56–58; *J. S. C. I.*, 1894, p. 26).

To obtain the best lighting or heating effects, the apparatus must be adapted to the gas. By ignoring this, either as regards lighting or heating burners or gas-engines, misleading results may be obtained.

From an economic point of view each candle unit costs so much, and it is a question of price whether the extra candle of 16 over 15 candle gas, or of 17 over 16, &c., is worth the additional cost of production. If the heating power marches with the lighting power, the same consideration applies to the heating value.

* Read before the British Association (Section B), Bradford Meeting, 1900.

From a health point of view the less gas that can be made to supply the light required the better. The introduction of the incandescent and other improved burners show how much we have still to learn in obtaining light by the combustion of coal-gas.

The luminosity of the incandescent burner is largely an effect of high temperature rather than of quantity of heat, and I shall not refer to it further in this paper.

Coal-gas is a complex mixture, varying in composition with the coal distilled and the conditions of manufacture. Speaking broadly, it is a mixture of hydrogen and marsh-gas with smaller quantities of heavy hydrocarbons, oxides of carbon, aqueous vapour, nitrogen, &c.

In ordinary burners the lighting power depends chiefly on the heavy hydrocarbons. The heating value is also affected by these, but depends mainly on the marsh-gas and hydrogen, which form from 70 to 80 per cent of the gas.

In gas made from common coal, with a lighting value of 12 to 17 candles, the heating and lighting values march well together. If any material proportion of air is drawn into the gas before it is consumed, or if the gas first given off from the coal is collected separately from that given off last, the relations of heating and lighting powers are materially affected. Air or nitrogen in gas lowers the lighting power more than the heating power, whereas heavy hydrocarbons have an opposite effect. This latter consideration applies to gas enriched with light petroleum ("carburene") or with benzol, and explains why carburetted water-gas has a much lower heating value in proportion than coal-gas. In my own and other experiments its heating value is lower by at least 10 per cent than coal-gas of the same lighting power.

In gas made from the same kind of coal the heating and lighting powers march together, and a calorimeter kept constantly working may be used to watch the gas in place of a jet photometer. With mixed gases it would not be applicable, but in that case only a full photometric test would give the true lighting power.

Since gas has been so much used for heating, the measurement of its heating or calorimetric value assumes additional importance. Various calorimeters have been devised by Berthelot in France, Junker in Germany, and Dowson in this country.

The two latter are adapted for continuous working, and are very similar in principle and construction. In both, the products of combustion are made to pass through metallic syphons, so as to give up all their heat to a circulating current of water. Knowing the quantity of water heated during an experiment by so many degrees, the heat units are obtained, and, reading the volume of gas consumed during the experiment, the heat units per cubic foot of gas are calculated. In these instruments the steam produced by the combustion of the hydrogen in the gas is condensed into water. If it is desired to deduct the heat due to this condensation, the water is collected and measured. With such a large surface wet with the condensed water this correction can only be an approximate one. The amount of water obtained from gas of from 15 to 18 candles averages about 25 c.c. per cubic foot of gas, corresponding to 15 calories, or about 60 British thermal units.

The following average results have been obtained with coal-gas:—

Lighting power, English standard candles.	Heating power, British thermal units. (Pounds of water heated 1° Fahr., not corrected for steam condensed).
11	533
12	555
13	578
14	601
15	624
16	648
17	676
18	704

These numbers are comparable with those of Aguitton, but lower.

To obtain trustworthy results the following precautions are useful:—The calorimeter should be carefully shielded from draughts. The gas should pass through a very efficient governor, and the water supply should be as constant in pressure as possible, and should leave the calorimeter at a constant level, that of the top of the instrument. It is well to place a mirror under the burner so that the flame may be seen at any moment. The flame should be clear and steady, and no result should be accepted with a flickering or unsteady flame.

In starting the instrument it is often some time before a steady flame can be obtained, and for this reason the instructions sent out with the calorimeter, to turn off the gas at the meter at the close of an experiment, could be much improved by directing the gas to be turned into a bye-pass past the meter, so that the working of the calorimeter for the next experiment will not be interfered with.

ISOMORPHOUS DERIVATIVES OF BENZENE.*

THE existence of morphotropic relationships between the crystalline forms of substances which are not isomorphous in the formal sense of the term has of recent years acquired new importance, the purely geometrical work of Barlow (*Proc. Roy. Dub. Soc.*, 1897, viii., 527) and others having demonstrated the superfluity of the old view that the units of the crystalline structure are polymerides of the chemically active fundamental molecule as a means of explaining polymorphism and kindred crystallographic phenomena, whilst Fock (*Zeit. f. Kryst.*, 1897, xxviii., 337) has shown, from the study of the partition coefficients of two isomorphous substances in equilibrium in a liquid and a solid solution in contact, that in the case of salts, at all events, the molecular weight in the crystalline state may be that of the fundamental molecule. Moreover, the work of Paternò (*Gazzetta*, 1895, xxv., i., 411) and others on the cryoscopic behaviour of substances possessing constitutions similar to that of the solvent, indicates with certainty that isomorphism and morphotropy are phenomena which merge gradually one into the other.

The consideration of facts such as these leads to the conclusion that morphotropy and isomorphism have a common cause, and that this is more likely to be discovered by the crystallographic study of substances showing morphotropic relationships than from the examination merely of materials likely to exhibit isomorphism.

The benzene series offers exceptional opportunities for the study of such questions; indeed, it is remarkable that the publication of Groth's important memoir (*Pogg. Ann.*, 1870, cxli., 31), calling attention to the existence of morphotropic relationships between benzene derivatives, has not acted as an incentive to really systematic work on the subject.

The two investigations to be referred to form part of a series which are being carried on in the chemical department of the Central Technical College, South Kensington, in order, as far as possible, to determine the effect on the crystalline form of certain definite changes in the composition. The work will include the determination of the molecular volumes and of the melting-point curves of mixtures of the morphotropically related compounds.

Morphotropic Relationships between Formanilide and its Substitution Derivatives.

In order to determine the morphotropic effect of substitution upon the crystalline form of formanilide the simple anilides of the composition $C_6H_5.NH(CO.X)$

($X=H, Me, Et, Pr, \&c.$) as well as several of their alkyl-derivatives, and also a number of the mono- and di-halogen derivatives, have been crystallographically examined by Mr. L. P. Wilson; a list of the compounds measured is given in Table I., in which the geometrical constants are also indicated. It is evident that a progressive change in the structural dimensions occurs as each series is traversed, although in most cases this only becomes obvious on re-arranging the axial ratios, and sometimes on taking simple multiples of the ratios. The form in which the axial ratios are compared is indicated in the second column.

In Series I., although the first member is monosymmetric, whilst the others are orthorhombic, a well-marked morphotropic similarity in the magnitudes of the ratio a/b is observed to follow the displacement of the hydrogen atom in the acidic group by $Me, Et, \text{ or } Pr$. The effect of displacing the aminic hydrogen atom by $Me, Et, \text{ or } Pr$ is less, as is shown by an inspection of Series II.; in this case the ratio c/b is more nearly constant throughout the series than is the case in Series I. In Series III., obtained by displacing the acidic hydrogen atom in parabromofornanilide by either Me or Et , the ratio a/b again shows approximate constancy. No simple relationship is observable between parabromacetanilide and its methyl or ethyl derivative. Parabrom- and paraiod-acetanilide are isomorphous; the corresponding chloro-derivative is not isomorphous with them, although it bears a marked morphotropic relationship to them (compare Fels, "Dissert.," Leipzig, 1900). Group 6 forms a well-marked isomorphous series.

Otten (*Zeit. f. Kryst.*, xvii., 391) has observed that butyranilide is dimorphous, but has not examined the substance in great detail; a study of this compound has shown that the dimorphism is of a very remarkable character. At ordinary temperatures the anilide separates from alcoholic solutions in large transparent crystals of pyramidal habit, which are distinctly orthorhombic, showing a characteristically orthorhombic interference figure of small optic axial angle. The axial ratios of such crystals are $a:b:c=0.6920:1:0.6792$. On preserving crystals which had been measured at a constant temperature of 8° to 11° they have been found to change gradually, and in the course of three months completely, into tetragonal crystals, without at the same time losing their brilliancy and transparency. The axial ratio $a:c=0.6652:1$ in these crystals; they exhibit the characteristic uniaxial interference figure. On preserving the definitely tetragonal material at 30° for eighty days the reverse change occurs, the crystals becoming orthorhombic and biaxial, although the axial ratios never revert to quite their original values. The density of the orthorhombic form is 1.130, whilst that of the tetragonal form is 1.139.

The molecular volumes of several of the anilides have been determined, with the object of examining the relations between the optic axial ratios of Muthmann (*Zeit. f. Kryst.*, 1894, xxii., 497); the ordinary axial ratios seem, however, in most cases to express the morphotropic relationships just as clearly as the optic ratios.

Iso- and Polymorphous substituted Benzene-sulphonic Chlorides and Bromides.

It has already been stated (*B. A. Report*, 1899, p. 688) that the sulphonic chlorides and bromides derived from the 1:3:4 dihalogen-benzene-sulphonic acids together form an isotrimorphous series. Dr. Jee's further study of this group has led to important results. The series includes anorthic, orthorhombic, and monosymmetric terms, in the manner shown in Table II.

Of these eight substances, three are stable in the anorthic system, three in the orthorhombic system, and two in the monosymmetric system. Change of the one form into the other has been observed in four cases (IV., V., VII., VIII.) on allowing the fused substance to cool on a microscopic slide; the direction of the change in each case is indicated in the table by an arrow. A

* Report of the Committee, consisting of Professor H. A. Miers (Chairman), Dr. W. P. Wynne, and Dr. H. E. Armstrong (Secretary). Drawn up by the Secretary. Read before the British Association (Section B), Bradford Meeting, 1900.

TABLE I.

I.								β	
Formanilide	a : b	c = 2'188	: 1 : 2'403	90	54	M			
Acetanilide	c : b	a = 2'0670	: 1 : 0'8488	90		O			
Propionanilide	c : b	a = 2'1665	: 1 : 1'0428	90		O			
Butyranilide	3a : b	2c = 2'1663	: 1 : 1'3788	90		O			
II.									
Acetanilide	c : b	a = 2'0670	: 1 : 0'8488	90		O			
Methylacetanilide	2c : b	a = 0'7906	: 1 : 0'8494	90		O			
Ethylacetanilide	c : b	a = 1'0064	: 1 : 0'8401	90		O			
Propylacetanilide	c : b	a = 1'3264	: 1 : 0'8410	90		O			
III.									
P.-brom.-formanilide	c : b : 2a	= 1'4100	: 1 : 2'2056	90		O			
„ acetanilide	a : b : c	= 1'3904	: 1 : 0'7159	90		O			
„ propionanilide	3a : b : c	= 1'3400	: 1 : 0'8948	90		O			
IV.									
P.-brom.-acetanilide	a : b : c	= 1'3904	: 1 : 0'7159	90		O			
„ methyl acetanilide	a : b : c	= 1'5546	: 1 : 0'9719	70	7	M			
„ ethyl „	a : b : c	= 1'4063	: 1 : 1'5686	95	35	M			
V.									
P.-chlor.-acetanilide	a : b : c	= 1'3263	: 1 : 0'6804	90		O			
P.-brom- „	a : b : c	= 1'3904	: 1 : 0'7159	90		M			
P.-iodo- „	a : b : c	= 1'4185	: 1 : 0'7415	90	29	M			
VI.									
2 : 4-Dichlor.-acetanilide	a : b : c	= 0'8263	: 1 : 0'6828	77	33	M			
„ Chlorbrom.-acetanilide	a : b : c	= 0'8144	: 1 : 0'6722	77	40	M			
„ Bromchlor- „	a : b : c	= 0'8214	: 1 : 0'7074	77	46	M			
„ Dibrom- „	a : b : c	= 0'8131	: 1 : 0'6895	78	24	M			

TABLE II.

	Orientation.			Crystallographic systems.		
	1.	2.	3.	Anorthic.	Orthorhombic.	Monosymmetric.
I.	Cl	Cl	SO ₂ Br	Stable	—	—
II.	Cl	Br	SO ₂ Br	Stable	—	—
III.	Br	Cl	SO ₂ Br	Stable	—	—
IV.	Br	Br	SO ₂ Br	Labile→	Stable	—
V.	Br	Br	SO ₂ Cl	(Labile)→	Stable	Labile
VI.	Br	Cl	SO ₂ Cl	—	Stable	Labile
VII.	Cl	Br	SO ₂ Cl	—	Labile→	Stable
VIII.	Cl	Cl	SO ₂ Cl	—	Labile→	Stable

labile anorthic crystalline form of dibromo-benzene-sulphobromide (IV.) has been obtained from solution; and it has been found that each of the four sulphochlorides (V.—VIII.) can be caused to crystallise in the alternative system by admixture with a sulphochloride which usually separates in that system. It has been possible to determine the symmetry of all the forms referred to in the table by crystallographic measurement, with the single exception of the labile anorthic form of dibromo-benzene-sulphochloride, but the existence of this form is indicated by the dimorphous change which occurs on cooling from the melting-point to the atmospheric temperature.

The detailed study of such a series of isomorphs—especially of the melting-points of mixtures and of the conditions which determine the separation of the various crystalline forms—will be of importance, as it is likely to furnish information of value in discussing the phenomena presented by igneous rocks containing isomorphous minerals, and by alloys.

The investigation has been extended by Dr. Jee to the corresponding derivatives of the 1 : 3 : 5 dihalogen-benzene-sulphonic acids. The results obtained indicate the existence of an isodimorphous series having no apparent similarity with the 1 : 3 : 4 series. One of the members of this new series—1 : 3 : 5 dibromo-benzene-sulpho-

bromide—has been obtained in two distinct crystallographic forms, both belonging to the monosymmetric system. At atmospheric temperature one of these forms is labile and isomorphous with the corresponding sulphochloride, and with 1 : 3 : 5 bromo-chloro-benzene-sulphochloride. The stable form of 1 : 3 : 5 dibromo-benzene-sulphobromide, on the other hand, is isomorphous with 1 : 3 : 5 bromo-chlorobenzene-sulphobromide. The derivatives of the symmetrical dichloro-acid have not yet been satisfactorily measured.

Even in their present incomplete form these results are of considerable importance as showing the manner in which the occurrence of polymorphism may render obscure otherwise well-marked isomorphous or morphotropic relationships. Apparently a substance may crystallise in a whole series of different forms, A, B, C, D, the particular form obtained under ordinary conditions being the form stable at the temperature at which the crystals are grown. Another substance, the immediate homologue of the first in an isomorphous series, can also assume crystalline forms corresponding with A, B, C, D, &c., but the particular form stable at ordinary temperatures will not be the same as before, owing to the non-correspondence of the transition temperatures. Consequently the first member of an isomorphous series may crystallise in a

form of type A, the second member in a form of type B, the third of type C, and so on, the isopolymorphism completely masking the isomorphism.

RECENT RESEARCHES ON INDICAN.

By EDWARD SCHUNCK, Ph.D., D.Sc., F.R.S.

RECENT researches, chiefly by Dutch chemists, have thrown much light on a very interesting question, that of the state in which the colouring-matter of indigo exists in the cells of plants. Since the date of the publication of my researches (1855-56) very little attention had been paid to the subject, this being in a great measure due to the difficulties of the investigation, difficulties of which I myself had some experience, and which were reflected in the imperfect nature of my results. It was therefore with no small interest that I read the memoir of Prof. Hoogewerff and Mr. Ter Meulen, in which the authors describe their method of preparing a colourless crystalline glucoside in place of the amorphous indican, the only compound yielding indigo hitherto known (*Kon. Akad. v. Wetenschappen*, April, 1900). Though the existence of such a compound had been anticipated by Dr. Marchlewski and Mr. Ratcliffe, still its actual preparation was a meritorious achievement.

Mr. Hazewinkel has also published a memoir in the same journal as the preceding, in which he shows that indican, by decomposition with acids, enzymes, &c., yields indoxyl, which by subsequent oxidation is converted into indigo-blue. This might have been anticipated, since it was shown several years ago, by Dr. Roemer and myself, that indican in watery solution does not yield indigo-blue with acid, unless an oxidising agent, such as ferric chloride, is present at the same time.

Prof. Hoogewerff, of Delft, had the kindness to forward to me a small specimen of his indican, sufficient to enable me to confirm his account of its properties. My examination, however, though of course very slight, led to the conclusion either that my indican must have been very impure even for such a substance, or that there exists more than one substance to which the name has been applied. Assuming the last supposition to be correct, and giving the name *alpha-indican* to the original substance as described by me, and that of *beta-indican* to the substance of the Dutch chemists, I may indicate in a few words the distinguishing characteristics of the two as follows:—

1. *Alpha-indican* and *beta-indican* are soluble in water, alcohol, and ether.
2. The solutions of *alpha-indican* are coloured yellow on the addition of alkalis, and give yellow precipitates with lead acetate, while the solutions of *beta-indican* remain white with alkalis and give white precipitates with lead acetate.
3. By the action of strong acids and a mild oxidising agent *alpha-indican* yields indigo-blue, indigo-red, and a body which resembles but is not identical with glucose, inasmuch as it is not fermentable, while *beta-indican* with acid and ferric chloride is simply decomposed into indigo-blue and glucose.
4. By the action of caustic alkalis at a boiling temperature *alpha-indican* is changed and modified in some way, so as now to give with acids very little or no indigo-blue, but in its place indigo-red; whereas *beta-indican*, if I understand aright what Prof. Hoogewerff and Mr. Ter Meulen say, is not affected by the action of caustic alkali.

Anyone conversant with this department of Chemistry, and reading the description of the two bodies without prejudice, would probably come to the conclusion that they are distinct, not mere modifications of one substance. Of course it is easy to say that *beta-indican* represents

the pure substance deprived of the impurities accompanying it in the original substance; this is possible, and even probable, but not proven. To have obtained a comparatively stable crystallised substance in place of what previously represented it, which was amorphous and ill-defined, is a very meritorious piece of work, but it does not exhaust the question.

Anyone reading my early memoirs on this subject would see how carefully I avoided, in the preparation of indican, the use of an elevated temperature, even that of boiling alcohol. The extraction of the material, and the subsequent evaporation of the extracts, were made in the cold, because I convinced myself that, at a higher than ordinary temperature, indican, especially in watery solution, is modified so as no longer to yield indigo-blue on treatment. On the other hand, turning to the memoir of Messrs. Hoogewerff and Ter Meulen, we find them, in the preparation of their indican, employing boiling water, boiling alcohol, and even baryta water, all potent agents very likely to lead to metamorphosis in any body liable to change. In my opinion, therefore, the indican of Messrs. Hoogewerff and Ter Meulen is a derivative of *alpha-indican* or some similar substance, due to the action on it of agents apparently only employed for the purpose of purification. If I am asked how it is possible for a stable body like *beta-indican* to be derived from a very unstable body by the action of potent agents, I can only say I have no answer to give. I can only point to analogical cases; and of these I may mention that of chlorophyll. This body, when in solution, is very susceptible to the action of air and light, being rapidly bleached and decomposed thereby, but when its solutions are treated for even a short time with sulphuric or hydrochloric acid, products of decomposition are formed which are remarkably stable, resisting the action of air and light not for days only, but for weeks, and even months. The action of alkalis on chlorophyll leads, in a similar manner, to the formation of products of great stability. I have met with similar instances in other departments, such as that of the glucoside of madder, which, as my experiments prove, does not pre-exist as such in the plant; but I will not enter further on this at present. These facts have been strenuously denied by observers who choose to shut their eyes, but there can be no doubt of their reality for all that. And so in the case of indican as in that of chlorophyll, there may exist, before final decomposition takes place, intermediate products of which the final resultant products do not lead us to suspect the existence.

Prof. Beijerinck has thrown some doubt on the existence of indican in the leaves of *Isatis tinctoria*, and prefers to attribute the indigo-producing properties of woad to the presence of a body called by him *isatin*, which he has not isolated, and which, by the action of an enzyme called *isatase* present along with it in the plant, yields indoxyl, and then, by oxidation, indigo-blue. I confess I am at a loss to understand this view. Indican was first obtained by me from woad leaves, and the properties of the substance subsequently obtained from *Polygonum tinctorium* seeming to be precisely the same, I concluded the two were identical. I have repeated lately Prof. Beijerinck's experiment of passing air through an extract of woad leaves with boiling water, but no indigo-blue was precipitated until either a strong acid or an alkali was added, showing that if indoxyl was present in the extract it was certainly not in a free state.

In confirmation of this view, that woad leaves contain indoxyl either free or combined, Prof. Beijerinck states that if isatin be added to a watery extract of woad leaves, and the liquid be boiled, indirubin, or at all events a substance dissolving in alcohol with a bright red colour, is deposited. This does not, however, always take place. Sometimes the deposit does not consist of indirubin, but of a peculiar substance which I discovered many years ago on adding isatin to a boiling extract of woad leaves, though I am not sure that I have anywhere described it. This substance, when pure, appears in micro-

scopic crystals, and in mass is dark blue, almost black. It might be mistaken for indigo-blue were it not for the peculiar bronze-like (not coppery) lustre which it exhibits when rubbed with a hard body. It may be kept for years in a dry state, but if its alcoholic solution, which is bright blue, be left to stand only a few minutes, the colour changes to yellow, and the substance is completely metamorphosed. In acting on indican with acids some indirubin is always formed, but much more when the indican has been previously acted on by a caustic alkali, as I have pointed out on previous occasions.

The discordant results obtained by Dr. Marchlewski in his examination of indirubin would almost lead one to infer that there are several substances of similar properties comprised under the head of indirubin, from whatever source derived. The decomposition of indican, whether it be a glucoside or not, so as to yield indigo-blue as one of its products, has been ascribed by some to the action of microbes, by others to that of a peculiar enzyme. There is one process, however, observed by me which cannot, I think, be ascribed to either cause. It is as follows:—If a plant of *Polygonum* or of *Isatis* is immersed in a vessel of water, and the vessel is placed in a freezing mixture until the liquid has become one mass of ice, it will be found, after thawing, that the leaves that were thoroughly frozen will be found limp, flaccid, and discoloured, and, after treatment with boiling or even cold alcohol to remove the chlorophyll, those very parts will appear blue, sometimes a very dark blue, while the leaves and parts of leaves not affected by the excessive cold will be almost colourless. That the indigo-producing body of leaves should be changed in the same way, by exposure to unusual cold, as by the action of acids, alkalis, or ferments, is indeed strange, and cannot, in my opinion, be explained in any of the usual ways. Bacteria would seem in this case to be excluded, as it is difficult to conceive the possibility of their existing and acting within a block of ice. It may be surmised, too, that any plant-enzyme or enzymes would fare no better as agents of decomposition. No fermentation of any kind can take place at a temperature of 0°: this is conceded by all who have discussed the subject of fermentation. Some other cause must be found for the peculiar effect of cold which takes place equally in the case of *Isatis* and *Polygonum*, and must in both cases be the same. The same effect as by cold is produced by dipping the leaves of either plant into moderately strong alcohol, which on standing removes the chlorophyll, the leaves remaining more or less deeply coloured blue. This reaction has already been described by Prof. Beijerinck, but he has not, in my opinion, sufficiently explained it. I will not enter into speculations on this matter, as these would be more or less hypothetical.

Kersal, Manchester, October 10, 1900.

NOTES ON THE FERROCYANIDE TITRATION OF ZINC.*

By EDMUND H. MILLER and E. J. HALL.

THE experiments recorded in this article were undertaken to find out the influence of hydrochloric acid and those salts most likely to be present, on the estimation of zinc by titration with potassium ferrocyanide, using uranium acetate as an indicator.

The solutions used were:—

1. Potassium ferrocyanide, 43·2 grms. of the crystallised salt per litre.
2. Zinc chloride, 12 grms. (approximately) per litre, containing 40 c.c. of hydrochloric acid, 1·2 specific gravity.
3. Uranium acetate, a saturated aqueous solution.

The method and conditions of titration were as follows:—50 c.c. of the zinc chloride solution, containing 2 c.c. of hydrochloric acid, were measured into a beaker by a pipette; the salt, or acid, whose influence was to be tested, added; then water to bring the total volume to 200 c.c. The solution was then heated to boiling, and, after stirring vigorously, titrated. The conditions for titration, so far as volume and temperature are concerned, were in all cases 200 c.c. and 80°–90° C. The end point was determined in the usual way, using drops of uranium acetate on either sized paper, or on a porcelain tile. A light but distinct brownish flesh colour was taken as the end. The allowance necessary to turn the indicator in the presence of 2 c.c. of hydrochloric acid was found to be 0·3 c.c. on paper and 0·35 c.c. on porcelain. This difference is one of individual eyesight, and is given to explain why the quantities subtracted are not uniform.

Effect of Hydrochloric Acid.

C.c.	C.c.
2 HCl 1·2 sp. gr. required	0·35 K ₄ Fe(CN) ₆ solution.
4 " " "	0·45 " "
6 " " "	0·60 " "
8 " " "	0·75 " "
10 " " "	0·85 " "

Each result is the average of three determinations made on porcelain. More hydrochloric acid exerts such a solvent action on the uranium ferrocyanide as to render the indicator unreliable.

C.c.	C.c.	C.c.
50 ZnCl ₂ solution containing 2 HCl required	27·65	
50 " " "	4 " "	27·70
50 " " "	6 " "	27·80
50 " " "	8 " "	27·90
50 " " "	10 " "	28·00
50 " " "	12 " "	28·10
50 " " "	14 " "	28·20

Correcting by blank test we get that 50 c.c. of the zinc chloride solution containing 2 c.c. of hydrochloric acid requires 27·3 c.c. of the ferrocyanide solution. This is the result of six determinations, and is the value used throughout. The other results are averages of two or three tests. By subtracting 27·3 from the values given we get the amounts required for the indicator in the presence of zinc to be, for 4 c.c. HCl, 0·4 c.c.; 6 c.c. HCl, 0·5 c.c.; 8 c.c. HCl, 0·6 c.c.; 10 c.c. HCl, 0·7 c.c.; 12 c.c. HCl, 0·8 c.c.; 14 c.c. HCl, 0·9 c.c. Determinations made on paper gave slightly lower results: 6 c.c. HCl, 0·45 c.c.; 8 c.c. HCl, 0·5 c.c.; 10 c.c. HCl, 0·6 c.c.

These results show the great influence of hydrochloric acid on the indicator, and that it is diminished by the presence of zinc ferrocyanide.

Effect of Magnesium Sulphate.

Moldenhauer (*Chem. Zeit.*, 1891, No. 14) states that in the titration of zinc by potassium ferrocyanide in an ammoniacal solution magnesium interferes, as the ferrocyanide is not readily soluble in ammonia. The following tests were made to ascertain whether it had any influence in an acid solution. To 50 c.c. of the zinc chloride solution containing 2 c.c. of hydrochloric acid, different quantities of MgO as sulphate were added, and the solution titrated under the standard conditions.

0·01 gm. MgO required	27·65 c.c., corrected	27·35 c.c.
0·10 " " "	27·70 " "	27·40 " "
1·00 " " "	27·70 " "	27·40 " "

In order to test the solvent effect of magnesium sulphate on the indicator, two portions of crystallised magnesium sulphate, 6·111 grms. each (1 gm. MgO), were dissolved and titrated in the presence of 2 c.c. of HCl. They each required 0·6 c.c.

* Contribution from the Havemeyer Laboratories, Columbia University. From the *School of Mines Quarterly*, xxi., No. 3.

Assuming that the solvent action is less in the presence of zinc, as is the case with hydrochloric acid, we conclude that the interference of magnesium is negligible in an acid solution, and is due to a slight solvent action on the indicator, not to the formation of magnesium ferrocyanide.

Effect of Calcium Chloride.

The following weights of calcium chloride were added to portions of zinc chloride solution as described under magnesium sulphate:—

0.05 grm. CaCl_2 required	27.65 c.c., corrected	27.35 c.c.
0.50 " " "	27.85 " "	27.55 "
5.00 " " "	28.00 " "	27.70 "

Our experiments accord with the statement by Low (*Journ. Am. Chem. Soc.*, 1893, p. 552), that calcium acetate exerts a solvent action on uranium ferrocyanide, and so interferes in the lead titration by potassium ferrocyanide.

Effect of Ammonium Chloride.

As small amounts of iron are usually separated from zinc, in the analysis of ores, by the ammonia in the presence of a large amount of ammonium chloride, the effect of this salt is of importance. To 50 c.c. of zinc chloride solution containing 2 c.c. of hydrochloric acid, the following weights of ammonium chloride were added before titration under the usual conditions:—

5 grms. NH_4Cl required	27.85 c.c., corrected	27.55 c.c.
10 " " "	27.90 " "	27.60 "
20 " " "	28.00 " "	27.70 "

Tests were next made to see whether the error was due to a solvent action on the indicator. Ten grms. NH_4Cl added to 2 c.c. of HCl and titrated as usual gave a sharp end-point at 0.3 c.c.; 20 grms., the same result, 0.3 c.c., showing that the effect of large quantities of ammonium chloride was to sharpen the end-point (compare Beringer, "Text-book of Assaying," p. 221). That the influence of ammonium chloride is on the zinc ferrocyanide and not on the indicator is shown by the marked difference in the appearance of the solution titrated when ammonium chloride is present. The precipitate is greenish white and flocculent at the beginning of the titration; near the end, when about 0.3 c.c. more is required, as indicated by uranium acetate, there is a sudden change—the precipitate becomes brownish white and the green colour entirely disappears.

To confirm our results the following tests were made:—

NH_4Cl .	ZnCl_2	HCl.	Change in precipitate.	Vol. used.		Corrected.
	solution.			C.c.	C.c.	
0	50	2	None	27.65	27.30	
5	50	2	27.5	27.70	27.40	
10	50	2	27.4 (about)	27.80	27.50	
10	50	2	27.5	27.70	27.40	
20	50	2	27.6	27.85	27.55	

This change apparently coincides with the complete conversion of the zinc to $\text{K}_2\text{Zn}_3\text{Fe}_2(\text{CN})_{12}$. It does not take place when the titration is made in an ammoniacal solution, where the normal zinc ferrocyanide, $\text{Zn}_2\text{Fe}(\text{CN})_6$, is formed.

Effect of Aluminium Sulphate.

The removal of copper from zinc ores can be readily effected by aluminium foil in a sulphuric acid solution (Furman, "Manual of Practical Assaying," p. 209), but the uncertainty of the end-reaction with uranium acetate suggested the following experiments:—To 50 c.c. portions of the zinc chloride solution containing 2 c.c. of HCl, 0.20 grm. of Al_2O_3 was added in the form of crystallised aluminium sulphate. The amount of hydrochloric acid was varied.

Al_2O_3 .	HCl.	Volume used.		Corrected.	
	C.c.	C.c.	C.c.	C.c.	C.c.
0.20	2	22.80	22.50		
0.20	3	22.30	21.95		
0.20	5	26.80	26.40		
0.20	7	28.40	27.95		
0.20	7	27.75	27.35		
0.20	7	28.60	28.15		
0.20	7	28.00	27.55		

The influence of aluminium sulphate is very marked, giving low results with small amounts of acid, and in all cases irregular results. In the presence of this salt it is impossible to ascertain the end-point with certainty, as the brown colour appears very gradually and is never distinct.

Experiments were made with no zinc present which gave with 2 c.c. and with 6 c.c. of HCl, 0.7 c.c. as the allowance for the indicator, but the colour was not satisfactory.

When potassium ferrocyanide is added to a neutral solution of aluminium sulphate, the aluminium being in excess, and boiled, a white precipitate is formed, similar in appearance to zinc ferrocyanide; a drop of the solution containing this precipitate gives a brown colour with uranium acetate. When hydrochloric acid is added to the solution containing the precipitate, the reaction with uranium acetate is checked. A precipitate is formed on heating a solution of aluminium sulphate with potassium ferrocyanide, even in the presence of considerable hydrochloric acid.

The interference of aluminium with the indicator seems analogous to that of manganese (Stone, *Journ. Am. Chem. Soc.*, 1895, xv., p. 473) and is sufficiently marked to render its use for removing copper very objectionable.

Effect of Lead Chloride.

If we discard the use of aluminium to precipitate copper, we must go back to lead as the best substitute. The following experiments were made to determine how much hydrochloric acid is necessary to prevent any precipitation of lead ferrocyanide. The titrations were performed under the usual conditions, the lead being added as chloride to the zinc solution.

Pb.	HCl.	Volume required.		Corrected.	
Grm.	C.c.	C.c.	C.c.	C.c.	C.c.
0.005	2	27.70	27.40		
0.01	2	27.75	27.45		
0.02	2	27.80	27.50		
0.04	2	27.90	27.60		
0.08	2	28.00	27.70		
0.16	2	28.05	27.75		
0.32	2	29.60	29.30		
0.64	2	37.10	36.80		

Two c.c. of hydrochloric acid is insufficient for more than a trace of lead.

Pb.	HCl.	Volume required.		Corrected.	
Grm.	C.c.	C.c.	C.c.	C.c.	C.c.
0.32	4	27.90	27.55		
0.64	4	29.00	28.65		
0.32	6	27.85	27.40		
0.64	6	27.90	27.45		
0.32	8	27.95	27.45		
0.64	8	27.95	27.45		
0.32	10	28.00	27.40		
0.64	10	28.05	27.45		

This shows that 6 c.c. of hydrochloric acid, 1.2 sp. gr., will prevent any interference due to lead. As Comey's "Dictionary of Solubilities" states that lead ferrocyanide is soluble in sodium citrate, we tried this salt to prevent the precipitation of the lead, but found that, while it prevented the precipitation of lead, it had such a solvent action on uranium ferrocyanide that it could not be used. Citric acid was also tried without satisfactory results.

Effect of Bismuth Nitrate.

Small quantities of bismuth as nitrate were added to the zinc chloride solution and titrated as usual.

Bi.	HCl.	Volume required.	Corrected.
Grm.	C.c.	C.c.	C.c.
0.005	2	27.80	27.50
0.01	12	28.00	27.40
0.02	12	28.00	27.40
0.04	12	28.00	27.40

Small amounts of bismuth have no influence.

Effect of Antimony Trichloride.

0.10 grm. of antimony trichloride was added to the zinc chloride with sufficient acid to prevent the precipitation of basic salts.

SbCl ₃ .	HCl.	Volume required.	Corrected.
Grm.	C.c.	C.c.	C.c.
0.10	8	28.2	27.7
0.10	10	28.4	27.8

Antimony interferes with the titration.

We conclude from these experiments:—

1. That the amount to be subtracted, as shown by a blank test, is often greater than the excess required in the actual titration.

2. That salts (such as calcium chloride, sodium citrate) and acids (notably hydrochloric) retard the end-reaction by their solvent action on uranium ferrocyanide.

3. That ammonium chloride, not exceeding 10 grms., does not interfere with the accuracy of the method, but has some (unknown) effect on the zinc ferrocyanide.

4. That the presence of considerable quantities of aluminium sulphate—such as would be present if copper were removed by aluminium foil—renders the results unreliable.

5. That 6 c.c. of concentrated hydrochloric acid is sufficient to prevent any interference by lead.

6. That antimony gives high results, while small quantities of bismuth have no influence.

THE FORMULA OF COBALT PEROXIDE.

By THOMAS BAYLEY, Assoc.R.C.Sc.

A PAPER by Mr. T. Moore on the separation of nickel and cobalt appeared in the CHEMICAL NEWS of August 17th (vol. lxxxii., p. 73), in which he referred to the formula of the peroxide of cobalt precipitated by means of hypochlorites, hypobromites, &c., and incidentally mentioned the formula Co_3O_5 assigned by myself to the peroxide of cobalt in 1879 (*Proc. R. I. A., Journ. Chem. Soc.*).

The method by which the composition of this oxide, and of Ni_3O_5 , was determined was similar to that used by Mr. Moore, namely, dissolution of the washed peroxide in a liquid containing an acid and potassium iodide and titration of the liberated iodine with thiosulphate. But since the majority of dictionaries and text-books have not adopted the formulæ Co_3O_5 and Ni_3O_5 , in spite of subsequent confirmation of my results by other chemists, it occurred to me, about two or three years ago, to re-determine the composition of cobalt peroxide by a somewhat different method, and Mr. Moore's paper having recalled attention to the matter, the opportunity seems favourable for publication of the results so obtained.

The cobalt was weighed in the form of sulphate after careful ignition to low redness, which I have found to be one of the best forms in which to weigh both this metal and nickel. After precipitation, the peroxide was washed on an asbestos filter, and then dissolved in dilute sulphuric acid in presence of a known excess of ferrous sulphate, and the amount of Fe remaining unoxidised determined with standard potassium bichromate.

The general result of these experiments seems to be that, at ordinary temperatures, both chlorine and bromine in presence of caustic soda precipitate an oxide of the form Co_3O_5 , and that at 100°C . a lower—and perhaps rather less definite—form (which may be Carnot's $\text{Co}_{10}\text{O}_{16}$) is produced. The action of peroxide of hydrogen at the ordinary temperature is much less definite. The writing of the various formulæ in terms of Co_{60} is merely for purposes of convenient comparison.

$\text{CoSO}_4 = 464$ Grms. was taken for each Experiment.

	Fe oxidised. Grm.	Formula indicated.		Conditions of experiment.
1.	0.1855	$\text{Co}_{60}\text{O}_{93.2}$	$\text{Co}_{60}\text{O}_{93} = 9\text{CoO}, 11\text{CoO}_2$ requires 0.1841 grm.	NaHO and NaClO; and mixture heated to 100°C . (boiled).
2.	0.1832	$\text{Co}_{60}\text{O}_{93.8}$	Do.	Do.
3.	0.2258	$\text{Co}_{60}\text{O}_{100.4}$	$\text{Co}_{60}\text{O}_{100} = \text{Co}_3\text{O}_5$ re- quires 0.2232 grm.	NaHO and NaClO at ordinary temperature = 15°C .
4.	0.2243	$\text{Co}_{60}\text{O}_{100.2}$	Do.	Do.
5.	0.2218	$\text{Co}_{60}\text{O}_{99.7}$	Do.	NaHO and NaBrO at ordinary temperature.
6.	0.2172	$\text{Co}_{60}\text{O}_{98.9}$	Do.	Do.
7.	0.1347	$\text{Co}_{60}\text{O}_{84.1}$	$\text{Co}_{60}\text{O}_{84} = \text{Co}_5\text{O}_7$ requires 0.1339 grm.	NaHO + H_2O_2 at ordinary temperature.
8.	0.1109	$\text{Co}_{60}\text{O}_{79.9}$	$\text{Co}_{60}\text{O}_{80} = \text{Co}_3\text{O}_4$ requires 0.1116 grm.	Do.
9.	0.1878	$\text{Co}_{60}\text{O}_{93.6}$	$\text{Co}_{60}\text{O}_{93} = 9\text{CoO}, 11\text{CoO}_2$ requires 0.1841 grm.	NaHO + NaBrO, and mixture heated to 100°C . (boiled).
10.	0.1931	$\text{Co}_{60}\text{O}_{94.6}$	$\text{Co}_{60}\text{O}_{95} = \text{Co}_{12}\text{O}_{19}$ re- quires 0.1953 grm.	Do.; but scarcely raised to boiling.
11.	0.1897			NaHO and NaBrO, after boiling for thirty minutes.
12.	0.0942			AmHO and H_2O_2 , boiling.

The separation of the precipitated Co_3O_5 (hydrated) by filtration seems to be quite unnecessary; even in the cold the excess of hypochlorite being quickly decomposed by catalytic action, with evolution of oxygen; and if, after this has ceased to come off, iodide of potassium be added, followed by excess of hydrochloric acid, and the liberated iodine be titrated with thiosulphate and starch indicator, a measure of the cobalt is obtained.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART IV. NICKEL AND COBALT.

By HARRY BREARLEY.

(Continued from p. 43).

The arrangement of items is similar to that of the previous parts, *i.e.*, Separations, Estimations, Detection, and Miscellaneous Notes, and journals to end of 1899.

NICKEL.

I. SEPARATION OF IRON.

1. *By means of Acetates.*—The separation of nickel from iron by means of acetate requires greater manipulative precision than the like separation of any other element of the same group, and therefore a few references to papers which discuss the basis of acetate separations are included.

493. MACKINTOSH (C. N., lvi., 65).—Acetate separation needs to be repeated six times. Cobalt more difficult to separate than nickel. Precipitates Ni, Co, and Fe as sulphides, treats precipitate with HCl, and makes acetate separation of the soluble and insoluble portions.
494. WESTERSON (Z. I. S. I., 1894, ii., 495).—Sample dissolved in H_2SO_4 , oxidised, and Fe repeatedly precipitated. Mn interferes with electro-deposition of Ni.
495. BREARLEY (C. N., lxxiv., 16).—Precipitation from a solution containing 7 per cent acetic acid. Ni titrated with KCN and AgI; copper separated as sub-sulphocyanide; SO_2 and KCNS do not interfere with titration of the Ni.
496. DEBRAY (C. N., xxi., 53).—Ferric acetate separates on boiling into acetic acid and colloidal oxide; the latter is insoluble in ammonium salts and acetic acid.
497. BREARLEY (C. N., lxxvi., 222, &c.).—Ease of separation of the following elements is in the order Mn, Zn, Co, Ni. Attempts to deduce reasons for this from the character of the salts separated. Separation of various elements without a second precipitation (C. N., lxxvi., 49 and 222, Nickel; lxxvi., 165, Cobalt).
498. GIBBS (C. N., xi., 102).—Add enough acetate to convert all bases into neutral acetates to the cold solution.
499. BREARLEY (C. N., lxxix., 193).—It is best, according to both theory and practice, to add acetate to the boiling solution. (See also 1, 3, 4, and 8).

I. 2. Precipitating Iron as Hydrate.—

500. THOMAS (C. N., xxxv., 187).—Repeated precipitation of the Fe with excess of ammonia.
501. SLEEPER (C. N., lxi., 15).—Decompose material with aqua regia, KBr and Br, or NaHSO_4 . Precipitate Ni and Fe with NaHO, dissolve in H_2SO_4 , and rapidly add $(\text{NH}_4)\text{HO}$ to the cold solution. Detailed instructions for electro-deposition of the Ni.
502. NEUMANN (Z. I. S. I., 1898, ii., 560).—The Fe is separated with $(\text{NH}_4)\text{HO}$ and $(\text{NH}_4)_2\text{SO}_4$, and the Ni electro-deposited from the filtrate.

503. MOORE (C. N., xlv., 76).—To faintly acid solution add $(\text{NH}_4)_2\text{SO}_4$ and large excess oxalic acid; precipitate Fe with $(\text{NH}_4)\text{HO}$ (see 525).
504. EMMENS (Z. I. S. I., 1893, i., 414).—Precipitated ferric hydrate boiled with dilute acid; only little Fe dissolves along with the Ni; Ni and Co are electro-deposited. Applied to regulus, minerals, and alloys (Z. S. C. I., 1892, 1035).
505. JUPTNER (Z. I. S. I., 1894, i., 616).—Precipitate with $(\text{NH}_4)\text{HO}$ in the presence of $(\text{NH}_4)\text{Cl}$, and keep hot several hours. (Repeated precipitation is necessary, Z. I. S. I., 1894, ii., 495). Ni and Co precipitated as sulphides, and Mn and Al separated.
506. MOORE (C. N., lxx., 75).—The separation by NH_4HO^* is worthless; by acetate needs four precipitations. (See also 10, 14, 15, 19a, 21, 22, 23, 26).
507. BLOXAM (C. N., lli., 109).—The precipitation of Fe with $(\text{NH}_4)\text{HO}$ always carries down the Co in larger proportion than the Ni, so much so that Ni may in this way be roughly detected in the presence of cobalt.
508. REINITZER (C. N., xlviii., 114).—Solutions of Cr_2O_3 when boiled with soda acetate are not precipitated by alkalis, alkaline carbonates, phosphates, &c., and the same property is conferred on certain amounts of Fe or Al present therewith.
RECOURA (C. N., lxxviii., 46).—The presence of alkaline sulphites have a like effect.

I. 3. By Precipitating the Nickel.—

509. THOMPSON (C. N., vii., 185).—To acidulated sulphates of Ni, Co, Fe, Mn, Zn, and Cu add $(\text{NH}_4)_2\text{SO}_4$; nearly all the Ni and Co separate as "alums" on standing.
510. MOORE (C. N., lvi., 3).—Add pyrophosphate until precipitate begins to re-dissolve; add excess KCN, boil, add KHO, and precipitate Ni with KHO and Br. Co remains with the iron; Ni estimated electrolytically. A modified process leaving out pyrophosphate and embracing other separations (C. N., lvii., 125).
511. CAMPBELL and ANDREW (Z. I. S. I., 1895, ii., 598).—Add soda pyrophosphate and soda carbonate; precipitate Ni with soda xanthate; convert to sulphate and electro-deposit, or titrate with KCN and AgI.
512. PINERUA (C. N., lxxv., 193).—Based on the insolubility of the chlorides of Ni and Al and the solubility of the chlorides of Co and Fe in etherised HCl are processes for the separation of Ni and Al from Fe and Co (see 623 and 526).
513. PERILLON (Z. I. S. I., 1898, ii., 562).—Precipitate the dissolved sample with KHO, add oxalic acid, dry at 80° ; boil dried mass with a dilute acetic acid and alcohol, and ignite the precipitated oxalate to NiO .
514. CLASSEN (C. N., xxxvi., 40).—In Wöhler's process for separating As and Ni (544), if Fe is present the Co and Ni are completely precipitated on neutralising, adding acetic acid, and potassium oxalate (see 205).

I. 4. Electrolytic Separations.—

515. LE ROY (C. N., lxi., 194) and HERRENSCHMIDT and CAPELLE (C. N., lxi., 142).—Ni, Co, and Fe are deposited from a solution containing citric acid, ammonia, and ammonium sulphate; on reversing the current in an ammoniacal solution of $(\text{NH}_4)_2\text{SO}_4$, Fe is precipitated; Ni and Co are deposited together.

* In a private communication dated November, 1898, Moore speaks very highly of a separation with $(\text{NH}_4)\text{HO}$:—"I add an excess $(\text{NH}_4)\text{Cl}$ to the solution, then dilute to about 400 c.c. and carefully add (from a burette) dilute ammonia (1:15) until the Fe_2O_3 , &c., is precipitated. At this stage the solution is very distinctly acid, and the iron at least is perfectly thrown down. . . . I can vouch for its exactness for our (New Caledonian) Co and Ni ores."

516. DUCRU (C. N., lxxvii., 279).—Electrolyse ammoniacal solution containing precipitated iron. A small amount of iron is deposited with the Ni. Mn, P, and large amounts of Cr_2O_3 do not interfere. CrO_3 prevents electro-deposition entirely.
517. NEUMANN (Z. S. C. I., 1898, 1074).—On electrolysing as above (516) the deposited Fe varies with the amount in solution, time, strength of current, &c.
518. ENGELS (Z. C. S., lxxiv., ii., 192).—The deposited Ni is free from iron if the latter has been oxidized with H_2O_2 . (See also Foerster, Z. C. S., lxxiv., ii., 228).
519. VORTMANN (Z. C. S., lxxvi., 34).—Zn, Co, and Fe are deposited free from Ni in an alkaline tartrate solution. Ni, Co, and Cu are estimated in presence of Fe, and after the manner of 516.

I. 5. Miscellaneous Processes.—

520. MOORE (C. N., liv., 300).—Add soda phosphate, clear with acid, boil, and precipitate with acetate; precipitate Ni with KHO, and electro-deposit from sulphates. Shortcomings of Field's (22). Wöhler's (hydrate), and acetate processes enumerated.
521. CHENEY and RICHARDS (C. N., xxxvi., 161).—Acetate and hydrate inferior to Field's process. Precipitate with soda phosphate from acetic solution; Ni electro-deposited; with more than 3 per cent Ni, precipitation to be repeated.
522. EASTWICK (Z. I. S. I., 1894, i., 615).—Depends on solubility of nickel sulphide and insolubility of iron sulphide in acid solution of $(\text{NH}_4)_2\text{SO}_4$. A little Fe goes with the nickel.
523. GALBRAITH (Z. S. C. I., 1882, 345).—Precipitated with calcium sulphide; the Fe dissolved out with HCl; Ni weighed as sulphate.
524. ROSENBLATT (Z. C. S., i., 492).—Ni and Co are separated from Fe, Cr, Al, Mn, and Zn by precipitating the latter elements with potassium thiocarbonate.
525. ZIEGLER (Z. S. C. I., 1893, 377).—An acid solution of the metals is poured into an alkaline solution of ammonium borate. Ni, Co, and Cu are in solution; Fe, Al, and Mn are precipitated.
526. ROTHE (C. N., lxxvi., 182).—Hydrochloric acid solutions of ferric salts are soluble in ether; similar solutions of NiO, MnO, FeO, Cr_2O_3 , and Al_2O_3 are not; hence a means of separating them.
527. BREARLEY (C. N., lxxviii., 15).—Uses chromates instead of acetates. A large excess of the precipitant used in acetic solutions without any Ni being precipitated. Also separates Fe and Cu. (See also 10, 19a, 21, 22, 23, 25).

(To be continued).

PROCEEDINGS OF SOCIETIES.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

October 2nd, 1900.

Prof. HORACE LAMB, F.R.S., President, in the Chair.

MR. WILLIAM BURTON, F.C.S., gave a paper dealing with the question of "Plumbism" among pottery workers, from the technical point of view, showing how the plumbism was caused by the inhalation or swallowing of dust containing soluble lead compounds. It was pointed out that the abolition of lead from the glaze was not a practicable remedy, as leadless glazes suited to the conditions of the general run of English pottery are not yet within the reach of the manufacturers. Further, the abolition of lead from the glaze would not affect those cases which arise from the use of enamel or on-glaze colour used in

the form of dust or of spray, and no one has yet ventured to suggest that the use of lead fluxes for this purpose could be abolished.

The existing remedies in the shape of mechanical means for dealing with the dust in such a way that it should neither be swallowed nor inhaled, the periodic medical examination of the workers, and the proposed further safeguards of converting all the lead used into compounds of considerably lower solubility than those now employed, were also treated of.

The final opinion expressed by Mr. Burton was that the combination of all these safeguards would within a reasonable time render the operations of glazing and decorating pottery with substances containing lead compounds as free from risk to the operative as it was possible for any industrial occupation to be.

NOTICES OF BOOKS.

Fluorine and its Compounds ("Le fluor et ses Composés"). By M. HENRI MOISSAN, Member of the Institute. Paris: G. Steinheil. 1900. Pp. 397.

IN this volume the author has collected his numerous papers on fluorine and its compounds which have been published from time to time. Fluorine is a remarkable element, and has been too little studied; too great reliance has been placed on the parallelism of reactions, and the supposed analogy that new compounds of fluorine ought to have with the compounds of chlorine, bromine, and iodine. Fluorine, however, has special properties of its own which, though leaving it at the head of the halogen group, give it a place apart on account of the peculiarity of some of its characteristics.

At the commencement of his research the author directed all his efforts to the isolation of fluorine, and was thus enabled later on to have the command of large quantities of this gas.

New investigations then followed, such as the determination of some of the physical constants of fluorine, combinations with the metalloids and the metals, as well as organic compounds of fluorine.

In his recent investigations the author found it necessary to considerably modify the original form of his apparatus for producing pure fluorine. Its preparation is best effected by means of the electrolysis of hydrofluoric acid in a platinum U-tube, plunged into a vessel containing chloride of methyl; by this means the temperature is kept down to -23° . Owing, however, to the costliness of the platinum apparatus experiments were made with the object of replacing this metal by copper, and very good returns were obtained, though it was found necessary to retain platinum as the material from which the electrodes were made.

The general scheme adopted in carrying out the experiments with fluorine was as follows:—The bodies subjected to treatment with fluorine were divided into three classes—solid, liquid, and gaseous. When a solid body is to be treated a morsel may be placed in the delivery tube of the generating apparatus, or in the cover of a platinum crucible held in the stream of gas. When the substance under examination is a liquid, the fluorine may be simply passed through a glass tube in which the liquid is contained; the glass will not be readily attacked as it becomes protected by a thin layer of alkaline fluoride when the tube is dry, and if wet the moisture protects it; in some cases, however, when hydrofluoric acid is formed during the reaction, platinum tubes should be used. For examining closely the action of fluorine on a gas a special piece of apparatus has been devised; this is fully described and illustrated on pp. 82–83.

The author has again given the world a striking example of his patience and skill; his powers of descriptive writing

are of a high order, while his style and choice of language further help to stamp him as a *savant* of the first rank.

Tonometry ("La Tonometrie"). By F. M. RAOULT, Corresponding Member of the Institute, &c., Scientia Collection, No. 8. Paris: C. Naud. 1900. Pp. 116.

At the present day it is no longer possible for scientific men to become or remain specialists; it is imperative that they should be familiar with the ever growing extensions of the various branches of science; mathematicians, physicists, chemists, and biologists are all becoming more and more closely related, and have more and more interests in common.

The subject of the present monograph, "*Tonometry*," deals with the vapour tensions of liquid mixtures, of which one constituent at least is volatile; it is closely allied to cryoscopy, both having for their object the study of solutions.

The author first deals with solutions of organic substances or non-electrolytes, while in the second part he deals with solutions of mineral salts or electrolytes. There are several different methods of observation described, such as the static method, and the hygrometric, volumetric, and gravimetric methods; in the author's opinion, the method by boiling is, without question, the best of them all.

The book is handy in form, concisely written, and is decidedly worth reading.

CORRESPONDENCE.

THE PROPOSED NEW "SOCIETY OF CHEMICAL INDUSTRY OF VICTORIA."

To the Editor of the Chemical News.

SIR,—As a member of the Society of Chemical Industry, which Mr. H. W. Gepp, the Hon. Sec. of the Provisional Committee of the Victoria Society, terms the "English Society," may I be allowed to point out that the fourth paragraph from bottom of column 2, page 168, of your issue of October 5th, contains, to my thinking, no less than four somewhat misleading statements. These may be at once enumerated, and also corrected, as follows:—

1. Our Society is not, I think, an "English" Society merely; it is not merely a British Society; it is an Anglo-American Society. Its President of last session was an American, and I believe we are proud of both these facts.
2. Our Society was not established in 1882, but in 1881.
3. As to the Membership roll, the figure given—"over two thousand members"—would be more fairly expressed as "nearly four thousand members."
4. Membership of our Society has not only "proved a boon to chemists in London, Liverpool, Manchester, Nottingham, Glasgow," but also in the United States of America, and it seems somewhat strange that Mr. Gepp in his Circular should omit our most prosperous and rising Section, next to that of London, viz., the New York Section of the Society of Chemical Industry.

He probably would not have made the omission, however, had he been present at our Annual General Meeting this summer, and witnessed the enthusiastic reception accorded to our American President, and have heard his Address, and especially his speech at the Annual Dinner of the Society.

If there is one thing we of the Society of Chemical Industry are more proud of than another, it is of the fact that in the Society and its journal, the hands of British and American technical chemists are united—spite of the broad Atlantic—in a brotherly grip.—I am, &c.,

VERAX.

October 6, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal de Pharmacie et de Chimie,
Series 6, Vol. xii., No. 3.

Action of Nitric Acid on Trichlorised Gaiacol.—H. Cousin.—10 grms. of trichlorised gaiacol were dissolved in 50 c.c. of glacial acetic acid, and a mixture of 10 c.c. of nitric and 10 c.c. of acetic acid gradually added. The solution takes a brown colour, gives off reddish fumes, and after a time deposits a bright red crystalline powder. This product is purified by crystallisation in warm ether, and concentration of the ethereal solution. It is insoluble in water, soluble in alcohol, ether, acetic acid, and chloroform, especially when warmed; its fusing point appears to be between 158° and 162°. Analysis leads to the formula $C_{13}H_5Cl_3O_4$. The author then describes its behaviour with benzene.

Identity of *Bacillus Lactis Aerogenes* and the *Pneumobacillus* of Friedlaender.—MM. L. Grimbert and G. Legros.—The authors find that both biologically and morphologically, as well as in their action on carbohydrates these bacilli are identical, and they are therefore of the opinion that one name should suffice for both. Their principal characteristics are:—(1) Immobility; (2) the presence of capsules in the blood of inoculated animals; (3) the non-liquefaction of gelatin; (4) the non-production of indol; (5) the energetic action on the carbo-hydrates, giving rise to products variable with the nature of the sugar employed.

Estimation of Uric Acid.—A. Bellocq.—250 c.c. of urine are treated with an excess of soda and filtered; 200 c.c. of the clear filtrate are treated with 20 c.c. of a reagent consisting of 30 c.c. of 33 per cent pure sulphate of zinc, 30 c.c. of soda lye, and 40 c.c. of saturated carbonate of soda. A voluminous precipitate is formed and filtered off. This precipitate is dried in a crucible, and 2 or 3 c.c. of HCl (saturated with pure uric acid) added and kept cool; the crystals of uric acid soon sink to the bottom; these are removed by filtering through cotton-wool, dried, and weighed. The success of the operation depends on the first filtration.

Some Properties of Schinoxydase.—J. Sarthou.—The solubility of this substance is never complete, the filtration of its solution is very slow, and its reaction neutral. When evaporated to dryness it leaves a carbonaceous residue, which, when burnt with nitric acid and treated with water acidulated with hydrochloric acid, gives the reactions of salts of iron. The author describes an experiment showing that this metal exists in the organic state. Schinoxydase is soluble in acids, but all acids do not act in the same manner; traces of a mineral acid destroy the reactions of oxidation, which are slightly retarded by the presence of a small quantity of organic acids, though quite destroyed by a larger dose.

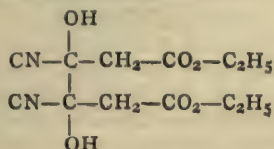
Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 11.

The Ammonio-earthly Phosphates.—L. Barthe.—Already inserted in full.

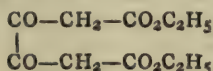
$\alpha\beta$ -Trimethyl- β -Oxyadipic Acid.—E. E. Blaise.—Already noticed.

Condensation of Cetipic Ether with the Orthodiamines. 1. Condensation with Ethylenediamine and the Naphthaleneorthodiamines.—R. Thomas-Mamert and St. Weil.—A very long paper, not suitable for abstraction.

Action of Hydrocyanic Acid on Cetipic Ether.—R. Thomas-Mamert and St. Weil.—The experiments here described were undertaken with the object of obtaining the dicyanhydrines of the formula—



by the fixation of two molecules of hydrocyanic acid on cetipic or oxalodiacetic ether,—



This fixation is not effected without considerable difficulty. After several unsuccessful trials it was found best to dissolve 1 molecule of cetipic ether in absolute alcohol, and then add a little more than 2 molecules of pure pulverised cyanide of potassium to the solution. To this mixture, cooled to 0°, the theoretical quantity of concentrated pure hydrochloric acid was added, drop by drop, with constant stirring. After some days a large quantity of a badly crystallised yellow body was formed: when no more cetipic ether is left, which is known by a small quantity evaporated to dryness giving no red reaction with perchloride of iron and a little alcohol, the solution is filtered. The ethereal filtrate on distillation leaves an oil from which fine crystals are obtained; these crystals, dried with blotting-paper and re-crystallised in alcohol, form large white plates, fusible at 164°, giving no reaction with perchloride of iron. This is the dicyanhydrine sought for.

New Colouring-Materials with an Acid Function.—M. Prud'homme.—The leucobase or chromogene colouring-materials, containing NH_2 groups, are treated in acid solution by a mixture of formic aldehyde and bisulphite of soda. The author gives the results of experiments with fuchsine, α -nitrodiaminotriphenylmethane, thionine, safranin, and nitraniline. He finds as he expected, that the mixture of CH_2O and SO_3NaH is without action on the colouring-matters of which the aminogenes are alcoylised, and also on the imidised bodies.

New Blue Colouring-Material, Solid with Alkalis, and of Special Constitution.—M. Prud'homme.—This new colouring-matter contains a SO_3H group in the ortho-position with regard to the central carbon; but instead of being connected directly with the benzenic radical, the SO_3H is connected to this radical by the intermediary of the $\text{NH}\cdot\text{CH}_2$ group.

Rhodinol and Citronellol.—L. Bouveault.—A controversial paper on the constitutional formulæ of these bodies.

The Transformation of Rhodinal into Menthone.—L. Bouveault.—Not suitable for abstraction.

Research on the Migrations and Metamorphoses of the Terpenic Compounds in Peppermint.—E. Charabot.—As a result of his observations, the author finds that menthol, which is formed at the commencement of vegetation, becomes partially etherified in the leaves; then when buds, and later flowers, are formed, a certain quantity of essence accumulates, and the menthol—both in the combined and free state—is converted into menthone by oxidation.

Influence of Active Vegetation on the Formation of Thuyone and Thuyol.—E. Charabot.—During the period of active vegetation not only the weight of the plant increases considerably, but the relative proportion of essential oil becomes almost double. A notable quantity of thuyol has been formed. This thuyol is trans-

formed partially into ethers, and partially into thuyone by oxidation.

The Presence of Cystine and Tyrosine in Contaminated Waters.—H. Causse.—Already noticed.

MISCELLANEOUS.

Merck's Digest, No. 9.—Stypticin.—This substance is a derivative of the opium alkaloid narcotine, obtained through the action of oxidising agents. The preparation forms a crystalline powder of the colour of sulphur; it dissolves freely in water, giving a straw-coloured solution; its formula $\text{C}_{12}\text{H}_{14}\text{NO}_3\text{Cl}$. In its chemical characteristics stypticin is closely allied to hydrastinin, which it also resembles in its physiological properties. Besides its powerful action in the stopping of bleeding, stypticin has, according to several medical authorities, a well-marked and potent sedative action, so that it is in every way to be preferred to the *extractum hydrastis liquidum*, and even to hydrastinin itself.

Experimental Research on New Explosive and Detonating Materials.—V. Alvisi.—This research has been carried out on the use of perchlorate of ammonium, mixed either with detonating gelatines, gelatinised gun-cottons, or even with mixtures of carbon and sulphur. The author has observed that for similar mixtures the explosion produces its maximum effect when the detonator itself contains perchlorate of ammonia mixed with the fulminate. Finally, the author has endeavoured to solve the problem of the commercial preparation of perchlorate. He has observed experimentally that the substitution of perchlorate of ammonia for the other oxidising salts in the actual explosives, or its addition to the substances which have no need of supplementary oxygen for total combustion, is capable of forming such mixtures as will give simultaneously (1) an increase in the ballistic force, (2) an increase in the disruptive force, and (3) an increase in the proportion between one and two; that is to say, mixtures which have the most advantageous properties, as mine explosives. The mixtures of perchlorate, sulphur, and carbon are made in various proportions; that of 5.5:1:1.13 appears to be one of the most useful. These mixtures have been named *mantianite*.—*Gazz. Chim. Ital.*, vol. xxxix., p. 121.

Some Double Thiocyanates of Vanadium.—A. Cioci.—*Thiocyanate of Vanadium and Potassium*,— $\text{Vd}(\text{CNS})_3 \cdot 3\text{KCNS} \cdot 4\text{H}_2\text{O}$.

This body is obtained by saturating a solution of SO_4H_2 and VdO_3 with SO_2 gas. After driving off the excess of SO_2 , the whole is reduced in a negative cell until no further green precipitate is produced with potash. The calculated quantity of thiocyanate is then added, and the product formed, insoluble sulphate of potassium, separated by means of alcohol. It consists of red crystals having a variegated appearance by reflected light, losing $4\text{H}_2\text{O}$ at 100° and decomposing at about 110°. The solution gives a precipitate of $\text{Vd}(\text{OH})_3$ with the alkalis, the alkaline earths, and their carbonates. A black precipitate is formed with CuSO_4 , a yellowish-red one with NO_3Ag , and a white one with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. *Thiocyanate of Vanadium and Ammonium*, $\text{Vd}(\text{CNS})_3 \cdot 3\text{NH}_4\text{CNS} \cdot 4\text{H}_2\text{O}$.—This body is obtained in a similar manner to the preceding one. It occurs in dark green crystals forming a blood-red powder. It behaves like the last compound. *Thiocyanate of Vanadium and Sodium*, $\text{Vd}(\text{CNS})_3 \cdot 3\text{NaCNS} \cdot 12\text{H}_2\text{O}$.—This body appears in greyish-red crystals, fusible at 68° in their own water of crystallisation. *Chromothiocyanate of Sodium*, $\text{CrNa}_3(\text{CNS})_6 \cdot 12\text{H}_2\text{O}$.—This body is obtained from sulphate of chromium and thiocyanate of sodium. It occurs in the form of bright red crystals, losing their water of crystallisation at 100°.—*Gazz. Chim. Ital.* (1), xxix., p. 300.

Action of Peroxide of Hydrogen on the Fatty Amines.—L. Mamlock and R. Wolfenstein.—In reading with peroxide of hydrogen on dipropylamine the authors have obtained dipropylhydroxylamine, $(C_3H_7)_2N.OH$, a white crystallised compound possessing an agreeable odour; on reduction it re-forms dipropylamine. In the same way as hydroxylamine gives sulphaminic acid when treated with sulphurous acid, so does dipropylhydroxylamine give dipropylsulphaminic acid. This acid turns litmus red; it does not contain either sulphurous or sulphuric acid, and corresponds to the formula $(C_3H_7)_2N.H.SO_3H$. When tripropylamine reacts with peroxide of hydrogen, oxide of tripropylamine is formed quantitatively. This oxide is deliquescent, and possesses basic properties. Its picrate, fusible at 130° , has been analysed. When the oxide is heated two reactions take place; on the one hand there is formation of dipropylhydroxylamine and propylene, and on the other hand regeneration of tripropylamine. When heated in vacuo this second reaction does not take place. The transformation of the oxide of tripropylamine into dipropylhydroxylamine has a certain interest in this sense, that this latter being easily reduced to dipropylamine, we have passed from a tertiary amine of the fatty series to a secondary amine.—*Berichte*, vol. xxxiii., p. 159.

MEETINGS FOR THE WEEK.

WEDNESDAY, 17th.—Microscopical, 8. "Report on the Recent Foraminifera of the Malay Archipelago," Part IX. At 7.30, Exhibition of Slides and Models of Skin Structure, by F. W. Watson Baker, F.R.M.S.

CITY OF BIRMINGHAM.

The SECRETARYSHIP of the GAS DEPARTMENT will shortly be vacant. Salary £1000 per annum. Preliminary enquiries as to the duties of the office should be addressed to the Secretary of the Gas Committee, Council House, Birmingham. Experience in the financial and commercial management of a Gas undertaking or of a large manufacturing business is desirable. Copies of applications for the appointment may be forwarded to members of the Gas Committee, but Candidates are earnestly requested to abstain from canvassing the members of the Council or of the Gas Committee.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2134.

AN IMPROVED DESICCATOR AND STIRRING-ROD.

By EDWIN DOWZARD, F.C.S.

EVERYONE has noticed, after placing a hot crucible in the desiccator, the jumping and side-slip of the lid; this is, of course, due to the expansion of the contained air, brought about by the hot crucible; when the crucible has cooled there is a slight vacuum, which renders the lid somewhat difficult to remove; when the lid has been removed there is a sudden inrush of air, which does not improve the efficiency of the desiccator.

Some desiccators have taps which may be opened and shut to allow for expansion and contraction, but the effect is the same, except that the lid does not slip and there is no difficulty in removing it; then there is the trouble of opening and shutting the tap every time the desiccator is used.

The following illustration (Fig. 1) shows how, in a very simple manner, the above faults may be remedied. The glass tube, A, is bent to fit inside the desiccator; the perforated plate, B, is raised sufficiently to allow the tube to pass underneath. It will be seen that this tube allows the ex-

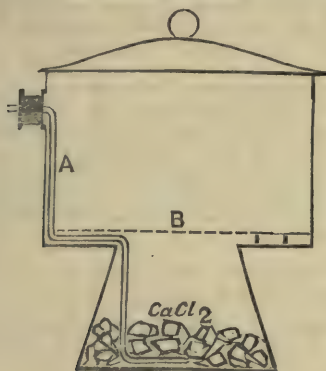


FIG. 1.

panded air to escape, and also allows air to enter, which has, however, to pass through and over the CaCl_2 contained in the lower part of the desiccator, thus ensuring a thorough drying.

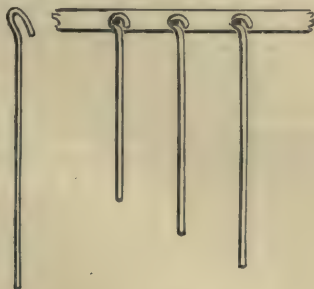


FIG. 2.

FIG. 3.

Fig. 2 represents an ordinary piece of glass tubing, sealed at both ends, one end being bent into a hook. By this means the rod may be suspended from a small nail

(see Fig. 3): the hook also acts as a handle when in use. The stirring-rod is thus always at hand, and the size needed can be selected without any trouble.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART IV.

NICKEL AND COBALT.

By HARRY BREARLEY.

(Continued from p. 181).

NICKEL (continued).

II. SEPARATING OTHER ELEMENTS FROM NICKEL.

Cobalt.—(See 598, &c.).

528. *Zinc*.—BRUNNER (C. N., i., 95).—With H_2S from solution containing soda acetate. Excess acetate and heat to be avoided. Ni and Co in solution.
529. DOHLER (Z. C. S., lxxv., 811).—Precipitate Zn with H_2S in the presence of soda formate and formic acid.
530. GIBBS (C. N., xi., 149).—Add HCN gas and Na_2S to solution containing acetate, or precipitate hot solution with Na_2S and dissolve out Zn with HCl. The former process also separates Ur from Ni and Co.
531. MOORE (C. N., i., 151).—Precipitate with $(\text{NH}_4)_2\text{S}$, dissolve in KCN, and precipitate ZnS with soda acetate and acetic acid.
532. VON BERG (C. N., lv., 236).—Precipitated with H_2S from formic or monochloroacetic solutions.
533. HAMPE (Z. C. S., lii., 182).—As 532. Monochloroacetic acid the more efficient, especially with Co.
534. BAUBIGNY (C. N., lix., 88).—From acetic solutions with H_2S in the cold. Not available for cobalt (Z. C. S., lvi., 653).
535. BEILSTEIN (C. N., xxxix., 74).— H_2S passed into cold ammoniacal solution made acid with citric; Zn precipitated. Electro deposition of Ni made from solution of nitrates; $(\text{NH}_4)\text{Cl}$ interferes.
536. ALT and SCHULZE (C. N., lxi., 124).—With H_2S from hot or cold solutions of succinic acid. Process for analysing nickel-silver. (See also 524, 573, and 574).
537. *Zinc and Copper*.—CARNOT (C. N., liii., 172 and 196).—Cu precipitated with hyposulphite. Zn from oxalic acid solutions with H_2S . Same process for cobalt.
538. WÖHLER (C. N., xxii., 84).—From acid solution of German silver precipitate Cu as CuCNS ; convert Ni and Zn to double cyanides; precipitate Zn with K_2S (not $(\text{NH}_4)_2\text{S}$), and Ni from oxidised filtrate with KHO.
539. MOORE (C. N., lii., 20).—Analysis of German silver. Precipitate Cu from HCl solution with H_2S , add KCN to filtrate, and precipitate Zn with $(\text{NH}_4)_2\text{S}$. The Cu and Zn are electro-deposited.
540. *Copper*.—DEWILDE (C. N., vii., 49).— H_2S always carries Ni down. Add cream of tartar, precipitate with KHO in alcohol, re-dissolve in excess, and precipitate Cu with glucose. The Ni, precipitated by KHO, after calcining and grinding, is easily washed free from potash salts.
541. RICKE (C. N., lxxvi., 241).—Ni-Cu alloys (coins) have the Cu deposited from acid solution of sulphates. Then Ni deposited from ammoniacal solution. Similar processes, ROBERTS (Z. C. S., i., 101) and LANGBEIN (Z. C. S., i., 1077).
542. CLASSEN (Z. C. S., xlviii., 191).—Cu electro deposited from ammonio-oxalates.
543. KAIKOW (Z. C. S., lxxviii., ii., 246).—Cu precipitated with hydrazine hydrochloride and KI. Ni, Cd, and Zn are in solution. (See also 578, 583).

544. *Arsenic*.—WÖHLER (*C. N.*, xxxv., 141).—Both metals precipitated with Na_2CO_3 digested with oxalic acid, and Ni or Co oxalates filtered off.
545. JANNASCH and LEHNERT (*J. C. S.*, lxx., ii., 547).—Co and Ni are precipitated from alkaline solution with H_2O_2 .
546. *Cadmium*.—SMITH and WALLACE (*J. C. S.*, lxii., 920).—Cd electro-deposited after adding KHO. Also RUDORFF (*J. C. S.*, lxiv., 305) and SMITH and MOYER (*J. C. S.*, lxiv., ii., 496). Ni is precipitated in acid solution if a strong current is employed.
547. *Bismuth*.—SMITH and MOYER (*J. C. S.*, lxiv., ii., 497).—Electrolytic. H_2SO_4 preferable to HNO_3 solutions.
548. JANNASCH and ROSE (*J. C. S.*, lxvi., ii., 482).—Separation in ammoniacal solution with H_2O_2 .
549. *Mercury*.—SMITH and FRANKEL (*J. C. S.*, lviii., 664).—Electro-separation of Hg and Ag from Ni and Co. Also HEIDENREICH (*J. S. C. I.*, 1896, 774) and RUDORFF (*J. C. S.*, lxvi., ii., 399).
550. *Gold*.—SMITH and MUHR (*J. C. S.*, lx., 1398).—Electro-separation from cyanide solutions.
551. *Aluminium*.—GONTIERE (*J. S. C. I.*, 1896, 830).—The metallic Al is dissolved in NaHO. The Ni is separated from the residual metals (Cu, Pb, Fe) by electrolysis and precipitation with ammonia.
552. LEFFLER (*C. N.*, lxxvii., 265).—Al precipitated with soda phosphate in acetic acid solutions.
553. *Lead*.—JANNASCH and LESINSKY (*J. C. S.*, lxvi., ii., 33).—Precipitated from ammoniacal solution with H_2O_2 .

III. GRAVIMETRIC ESTIMATION OF NICKEL.

III. 1. As Oxide or Sulphide.—

554. HADOW (*C. N.*, ii., 85).—Ni separated from solution of the ore with CaCO_3 and acetate; Ni and Co precipitated with H_2S and converted into sulphates, or precipitated with KHO or binoxalate and weighed as oxides. Filter-paper absorbs Ni and Co from strong solutions of the acetates.
555. GIBBS (*C. N.*, xvii., 172).—Ni is completely precipitated by a small excess of Na_2CO_3 and boiling. Ignited to oxide.
556. SCHMIDT (*C. N.*, lxx., 248).—Precipitated by H_2S from an $(\text{NH}_4)\text{NO}_3$ solution. The sulphide converted to oxide by ignition with ammoniacal mercuric cyanide.
557. ROSE (*C. N.*, ii., 302).—Neither Ni nor Co can be estimated as sulphide by heating with S in H, as iron, Mn, Zn, and Cu may.
558. FRESSENIUS (*C. N.*, iv., 150).— $(\text{NH}_4)_2\text{S}$ precipitates Ni slowly and not completely; $(\text{NH}_4)\text{Cl}$ assists, $(\text{NH}_4)\text{HO}$ retards, the precipitation.
559. LECREUIER (*J. C. S.*, lviii., 297).—The retention of nickel sulphide in solution is due to the formation of a thionickelate.
560. TERRELL (*J. C. S.*, lxii., 1132).— H_2S precipitates Ni and Co in the presence of many organic salts and sulphur and phosphorus acids.
561. BAUBIGNY (*C. N.*, xlv., 174 and 229).—Precipitation of NiO salts with H_2S depends on the ratio weight of acid to weight of metal, and not weight of acid to weight of water. This distinction serves to separate other metals (*e.g.*, Zn). (See also *C. N.*, xlv., 257). For action of H_2S on NiSO_4 in acetic solutions see *C. N.*, xlvi., 17; for action on NiCl_2 , see *C. N.*, xlvi., 40; action on Co salts, *J. C. S.*, liv., 113.

III. 2. By Electro-deposition.—

562. MERRICK (*C. N.*, xxiv., 100, 172).—Cu and Ni may be successively deposited from the same solution. Only a limited number of salts are suitable for electro-deposition (*C. N.*, xxvi., 209).
563. FRESSENIUS and BERGMANN (*C. N.*, xlii., 75).—Co and Ni not deposited if solution contains free mineral acids. Solutions of $(\text{NH}_4)_2\text{SO}_4$ (no NH_4Cl) are

best. Sulphocarbonate used to indicate when precipitation is complete.

564. RUDORFF (*J. C. S.*, lxiv., ii., 94).—From sulphate or pyrophosphate solutions.
565. CLASSEN (*J. C. S.*, xlviii., 191).—Ni, Co, and Fe deposited from double oxalates. Fe estimated volumetrically, Ni by difference; Co separated with nitrite.
566. BRAND (*J. C. S.*, lviii., 294).—From ammoniacal solution of the pyrophosphates.
567. KOHN and WOODGATE (*J. S. C. I.*, 1889, 256).—From various solutions. Table of metals which can be determined quantitatively, and references.
568. CLASSEN (*J. C. S.*, lxvi., ii., 481).—Particulars of current density, potential, &c., for deposition of Ni and other elements.
569. WOLMAN (*J. C. S.*, lxxiv., ii., 50).—Oxalate (565) and pyrophosphate (564) solutions lead to high results.
570. LANGBEIN (*C. N.*, lvii., 251).—The deposit from solutions containing Mn are contaminated thereby.
571. RICHE (*C. N.*, xxxvi., 96).—Deposition from ammoniacal solution carries down Mg. Purified by re-deposition.
572. ETTLE (*J. S. C. I.*, 1895, 69).—From ammoniacal solution of chlorides. (See also 501, 502, 504, 510, 520, 521).

III. 3. Miscellaneous Processes.—

573. FRESSENIUS (*C. N.*, xxix., 193).—Ore, &c., decomposed by acid or bisulphate, Schwarzenberg separation of Fe. Ni and Co precipitated with H_2S , with KHO, and finally reduced to metal in hydrogen. (See also *C. N.*, xxx., 16). Zn separated by volatilising with $(\text{NH}_4)\text{Cl}$, and Co as nitrate.
574. BAYLEY (*J. S. C. I.*, 1887, 449).—Add $(\text{NH}_4)_2\text{S}$ to alkalinity, ammonium benzoate, and HCl; the precipitated sulphide weighed as sulphate; Zn separated by a solution containing phosphoric acid.
575. CLARKE (*J. S. C. I.*, 1896, 866).—To solution containing ammonium phosphate add HCl to neutrality, then 20 per cent alcohol. Precipitate ignited to pyrophosphate. Zn is estimated similarly. (See also 632).

IV. VOLUMETRIC ESTIMATION OF NICKEL.

IV. 1. Titration with Potassium Cyanide.—

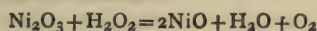
576. LECŒUVRE (*C. N.*, lxxi., 188).—Feebly alkaline solution titrated with KCN until the precipitate first formed just re-dissolves; NH_3 salts or small amounts of $(\text{NH}_4)\text{HO}$ do not interfere.
577. MOORE (*C. N.*, lix., 160).—Titrate in ammoniacal solution, using cupric ferrocyanide indicator. Sulphates, nitrates, chlorides, and acetates do not interfere.
578. CAMPBELL (*C. N.*, lxix., 139).—Fe separated as phosphate in acetic solution. Separate Cu with Pb, and then Pb and Mn as phosphate. Deposit Ni electrolytically or titrate with KCN, as in 577. How to prepare the indicator.
579. MOORE (*C. N.*, lix., 292).—Mn and large amounts of ammonium salts interfere with (577). By adding pyrophosphate to acid solution until precipitate re-dissolves and titrating ammoniacal solution, neither Fe, Al, Zn, nor Mn interfere.
580. DENIGES (*C. N.*, lxix., 42).—General method for estimation of Ag, in which KI is added to form indicator in ammoniacal solution. (This very suggestive paper should be read along with the processes for estimating Ni based on the same principle).
581. MOORE (*C. N.*, lxxii., 92).—KCN added until clearing of the suspended AgI indicates the formation of $\text{Ni}(\text{CN})_2 \cdot 2\text{KCN}$. The KCN may be standardised with Ni or Ag; Co is estimated with the Ni; Mn, Cu, and Zn interfere; Zn, Al, Fe, or Mg kept in

solution with pyrophosphate or an organic acid.*
(A good account of an admirable process).

582. BREARLEY and JERVIS (*C. N.*, lxxviii., 77, &c.).—Some points in the cyanometric estimation. Interferences exerted by a score elements, and means of avoiding them. Estimations in presence of elements giving precipitates in alkaline solutions. (See also 495, 511).

IV. 2. Miscellaneous Volumetric Processes.—

583. KUNZELL (*C. N.*, viii., 38).—Hot ammoniacal solution titrated with soda sulphide, using silver or nitro-prusside as indicator. Titration may be made in presence of Cu.
584. SYSSOFFEFF (*J. I. S. I.*, 1893, i., 414).—Precipitate Ni_2O_3 with Cl from a KCN solution; the Ni is calculated from the reaction—



after measuring the oxygen. Iron kept in solution as ferrocyanide.

585. GIORGIS (*J. C. S.*, lxxv., 452).—Gibbs's process, precipitating with alcoholic oxalic solution, is inaccurate. Precipitate with oxalic solution of Sr or Ba oxalate, and titrate either the dissolved precipitate or the excess of precipitant with permanganate.
586. LUCAS (*C. N.*, lxxx., 38).—Separate Fe with ammonia and $(\text{NH}_4)\text{Cl}$, add K sulphocarbonate, and compare red colour formed with standards; Co can be detected by using ammonium sulphocarbonate at the same time.
587. SPULLER (*J. I. S. I.*, 1897, ii., 507).—Fe precipitated with ZnO ; the filtrate colorimetrically compared with standards.

V. DETECTION OF NICKEL.

588. ALLEN (*C. N.*, xliii., 290).—Add $(\text{NH}_4)\text{Cl}$, $(\text{NH}_4)\text{HO}$, and ferricyanide; a red colour = Co; no change but a red precipitate on boiling = Ni. (See also CARTER, *C. N.*, xlvii., 273).
589. DAVIES (*C. N.*, xxxii., 44).—After detecting Co with ferricyanide, add ferrocyanide and HCl; a precipitate = Ni; detects 0.01 per cent; ferrocyanide may be used to detect Co also.
590. DONATH and MAYRHOFER (*C. N.*, xlv., 46).—Precipitate with NaHO and I, dissolve out Ni with ammoniacal $(\text{NH}_4)\text{Cl}$, and detect with $(\text{NH}_4)_2\text{S}$. Boil HCl solution of the residue with KHO; blue liquid = Co.
591. VILLIERS (*C. N.*, lxxi., 45 and 49).—Tartaric acid, NaHO , and H_2S added successively. The colour of the filtrate indicates traces of Ni.
592. CAVALLI (*J. C. S.*, lxxii., 603).—Precipitate with nitroprusside and treat with $(\text{NH}_4)\text{HO}$; only the Ni compound dissolves.

VI. MISCELLANEOUS NOTES.

593. PATTINSON (*C. N.*, viii., 136).—Ni and Co exist in small amounts in Cleveland ironstone.
594. WARREN (*C. N.*, lv., 37).—Certain metallic adulterations of cube Ni render the metal non-magnetic, and may thus be detected.
595. FLEITMANN (*C. N.*, lxx., 280).—Commercially pure nickel contains more or less Fe, Cu, Co, Zn, and Mn. Instructions for quantitative estimation of these.
596. CETTEL (*C. N.*, lviii., 48).—Analysis of nickel-silver and separation of Sn, Pb, Cu, Zn, Fe, and Mn. Ni electro-deposited.

* On this principle nickel is sometimes estimated in the Siemens steel bath, in about ten minutes, in order to find out how much of the rich ferro-nickel alloy must be added to bring the melt (which already contains nickel, due to scrap) up to the desired percentage. The KCN is standardised under the same conditions. Chromium interferes with the end-reaction.

597. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—Nickel is probably simply mixed with, or dissolved in, the iron.

(To be continued).

THE COMBUSTION OF ACETYLENE IN AIR ENRICHED WITH OXYGEN.

By G. L. BOURGEREL.

DURING the course of various researches carried out in the laboratory of the "Société Volta," at Geneva, I had occasion to seek for a source of high temperature other than that of the electric furnace, so that all electro-chemical action might be avoided in the reactions I had occasion to study. As the "Société Volta" were manufacturers of carbide of calcium, I naturally made use of acetylene, which is, further, in general use in the laboratory, and I made use of the burner of a table blowpipe, such as is commonly used for glass-blowing. By using compressed air, or air from a bellows, and acetylene, I produced a very high temperature, by means of which pure nickel or pure gold could be melted with ease. But as this temperature still did not satisfy my wants, I replaced the compressed air by pure compressed oxygen, which can now be easily obtained in cylinders.

Great, however, was my surprise to see that the flame leaving the blowpipe was exceedingly brilliant, and that, as a matter of fact, the gases did not mix, but burned only on contact one with the other, as in a lamp flame, forming a corona of flame, empty in the centre; then little by little there formed at the extremity of the central tube of the blowpipe a deposit of carbon which rapidly increased, taking the form of a truncated cone with the base outwards. This hollow cone, resembling a pear in shape, is formed of very dense carbon, very sonorous and hard at the base of the flame—that is to say, the point of the cone. It is so brilliant that at this point the outside appeared to be almost white, while all the wider portion and the interior has the appearance of very fine, light carbon, similar to lamp-black. Some individual cones were so hard at the narrow part that glass was easily scratched when fragments were rubbed on the surface with the aid of a cork.

The carbon thus deposited, when examined with a lens, has the appearance of an enormous number of cauliflowers crowded together. The inner side of this hollow pear is covered with a thin layer of lamp-black, and under this coating the carbon is perfectly bright and polished, hard, and of a steel-grey colour.

Its fracture is bright steel-grey at the lower portion, and becomes darker towards the large end; it is built up of superimposed layers, separated by very thin films of black, easily visible in the middle parts.

The very brilliant flame produced at the upper end of the cone is also very hot; on placing a piece of carbide of calcium the size of an egg in this flame it becomes red-hot, and fuses, while at the same time swelling up and throwing off on all sides incandescent particles, which continue to burn in the same manner as iron burns in oxygen; this makes a very effective experiment. The temperature of the acetylene which burns in the air round the end of this carbon cone, though not immediately in contact with it, is not very high; it is only at a nascent red-heat, and the examination of this flame quite justifies the theory of the dissociation of the acetylene at the moment of its combustion.

To return to the description of this curious experiment; as I did not want an incomplete combustion in my blowpipe, the idea occurred to me to return to the use of compressed air, and to introduce pure oxygen to enrich the air, by means of a branch tube joining the one which supplied the air.

In this manner the proportions of air and oxygen to each other and to the acetylene could be varied, and

flames of complete combustion produced having a neutral character, so to speak, neither oxidising or reducing; while, on the other hand, by increasing the amount of oxygen very hot oxidising flames could be obtained.

Thus in a non-luminous flame of this latter kind, a morsel of carbide of calcium became dissociated, losing its carbon, and becoming covered with a layer of fused carbonate of lime, a remarkable fact, while a small portion of the calcium is volatilised, and colours the flame red.

By using the blowpipe with a mixture of air and oxygen as I have described, we have at once a convenient source of intense heat, comparable with that of the electric arc, by means of which platinum itself can be melted in a few seconds, and which is free from the drawbacks inherent to the use of the electric arc, which is always reducing and carburising, and to the use of the oxyhydrogen blowpipe; both in commercial work as well as in the laboratory there are immense advantages to be gained by the use of such a source of heat.—*Moniteur Scientifique*, Oct., 1900.

ON OXYGEN IN STEEL.

By L. ROMANOFF.

ALTHOUGH the presence of very small quantities of oxygen has a very great effect on the resistance of steel to rolling, the estimation of this element is very rarely undertaken in metallurgical laboratories. It is important to determine the cause of the difficulties offered by this estimation, which takes a considerable time, and which requires the use of complicated apparatus.

Having had occasion to examine a certain number of samples of steel, burnt during the process of making in the Martin furnace, I decided to estimate the oxygen they contained. As a general rule, the quantity of air admitted to the hearth of the furnace is 10 per cent more than the theoretical amount, with the object of effecting complete combustion with the gases. In the Vacelet furnaces used by us, the gases ought to be consumed much more quickly, since the fuel (naphtha residues) is introduced direct, without any previous preparation. We can only achieve this by admitting as much as 25 per cent too much air into the furnace. At the commencement this method of working gave us burnt steels.

The method now in use of estimating the oxygen in steel was first due to Prof. Ledebur (*Stahl und Eisen*, 1882, p. 193). He made this estimation in various kinds of iron and steel, and determined the influence it exerted on the physical properties of the metal. Unhappily, since his time the progress made in this direction has been practically nil.

Two or three papers by Ledebur (*Stahl und Eisen*, 1883, p. 502; *Chem. Zeit.*, 1885, p. 17). A paper by Gladky (*Stahl und Eisen*, 1893, p. 293), and a few other odd papers (B. C. Calvert, *Comptes Rendus*, lxx., p. 453; Akerman, *Stahl und Eisen*, 1883, p. 149; Stummer, *Pogg. Anal.*, lxxxii., p. 136; Gruner, *Ann. Chim. Phys.*, Series 4, xxvi., p. 5; Platz, *Stahl und Eisen*, 1885, p. 471; Gladky, *Monit. Scient.*, 1889, p. 755) are the only literature we possess on this important question.

Before describing the methods we now have at our disposition for estimating the oxygen in steel, I must mention that all of them possess sources of error, and also entail very complicated manipulation. These methods may be divided into three groups:—

The first method depends on the property possessed by dry chlorine of acting on iron without touching its oxide. A current of dry chlorine is therefore directed on to some steel turnings or filings, so as to remove the iron in the form of chloride; unfortunately the residue does not consist entirely of oxide of iron—it also contains carbon, oxide of manganese, and a series of other compounds not attacked by chlorine.

The second method is founded on the use of a dissolving agent such as the sulphate or chloride of copper, iodine, bromine, bichloride of mercury, &c. Here again, however, the residue is not composed solely of pure oxide of iron; it also contains carbon, oxide of manganese, phosphorised and sulphurised compounds of iron, &c.

The third method, devised by Ledebur, consists of passing a current of pure dry hydrogen over steel turnings at a red heat, and weighing the water formed. It is, of course, necessary that the sample submitted to this treatment should be first made perfectly clean. If the metal contains a little oxide of manganese, that at once is a cause of error. The estimation of the oxide of iron in steel is of very great interest, since, according to Ledebur, it is this substance alone which possesses a deleterious action (Ledebur, *Moniteur Scientifique*, 1885, p. 732). In fact, according to this author, oxide of manganese occurs in melted steel solely in the form of a mechanical mixture, while the oxide of iron is in the dissolved state. By combining the third method with either of the two preceding ones we can obtain exact results; but such a proceeding would be extremely complicated, and could not well be carried out practically.

I must say a few words about another method, due to Tucker (*Iron and Steel Institute*, 1881, p. 205). It consists of mixing steel filings with powdered charcoal, and calcining the whole in a crucible. The steel is weighed before and after calcination, and the loss of weight represents the oxygen. Besides the fact that by this method we are obliged to use a very large sample (about 1 kilogramme), we are unable to take any account of the gases dissolved in the steel. This circumstance alone may falsify the results to the extent of 50 or even 100 per cent.

After having tried all the above methods, I came to the conclusion that Ledebur's (heating in a current of hydrogen) is the best; I, however, never first heated my samples in nitrogen; besides complicating the analysis without apparently affecting the results, I would point out that it is extremely difficult to prepare nitrogen absolutely free from oxygen. According to Ledebur the preliminary heating in nitrogen is to drive off the hydrocarbides with which the samples are always tainted, but without doing this I have obtained practically the same results as he did. Instead, I always wash the sample in alcohol and ether, and dry it in an exsiccator. In some special experiments, to which I shall refer later on, I did, however, have recourse to heating in nitrogen. As for the presence of hydrocarbides in the steel, during the heating in hydrogen, I do not attribute them to the oil present on the tool or file, but to a totally different cause, about which I shall have more to say further on.

I need not give detailed descriptions of the methods of drying and purifying the hydrogen and nitrogen. I will only say that I followed Ledebur's instructions closely. To the results obtained, and which are given in the following table, I have added a few observations on the behaviour of the metal while being filed. These remarks, though perhaps a little vague, are nevertheless worthy of attention.

I also thought it advisable to give the density of the different steels submitted to analysis, besides the estimation of the oxygen. I must here point out that the density is not so much influenced by the absolute quantity of foreign metalloids (especially oxygen) present as by the state in which this oxygen occurs in the metal, especially in the case of a Siemens-Martin or similar steel. In such a case, the bath of steel, which contains both carbon and oxygen at a very high temperature, cannot remain in a state of repose; the carbonic oxide is formed proportionally to the temperature and to the quantity of oxygen present in the charge. On cooling, the steel is unable to give off all this carbonic oxide, and there always remains therefore a certain quantity mechanically mixed: this will explain the slight variations which occur in the density of the metal.

In determining the densities I used crushed steel, which had passed respectively through two sieves of 1 m.m. and 2 m.m., so as to obtain grains of a uniform size. The grains were carefully stirred in water, after which the air was drawn off by means of a pump. I always used steel which had not been filed; this has the advantage of having a structure as uniform as possible.

No.	Per cent.					Density.	Effect of filing.	Elect. resistance.
	C.	Ph.	Mn.	S.	O.			
—	0.08	0.07	0.20	0.08	0.29	7.69	Crushed	—
496	0.107	0.04	0.57	0.03	0.19	7.79	Much heated	—
498.a	0.25	0.01	0.54	0.03	0.15	7.85	—	11.09
572.a	0.25	0.02	0.55	0.04	0.29	7.72	—	11.28
516.	0.10	0.04	0.50	0.07	0.11	7.92	Good	—
503.	0.10	0.08	0.55	0.06	0.25	7.84	Much heated	—
526.	0.095	0.02	0.37	0.06	0.22	7.78	—	—
540.	0.10	0.04	0.38	0.07	0.16	7.82	Flakey	—
547.	0.095	0.04	0.49	0.05	0.11	—	Good	—
550.	0.105	0.05	0.49	0.03	0.14	—	Rather heated	—
551.	0.09	0.06	0.32	0.04	0.16	7.87	"	—
553.	0.095	0.08	0.39	0.04	0.13	7.80	"	—
555.	0.10	0.05	0.44	0.03	0.13	7.87	"	—
570.	0.095	0.02	—	—	0.03	8.08	Good	—
581.	0.105	0.06	0.46	—	0.09	7.97	"	—
583.	0.10	0.04	0.42	0.03	0.02	8.08	"	—
616.	0.085	0.01	0.37	—	0.00	—	"	—
654.	0.11	—	—	—	0.00	—	"	—
576.	0.095	0.06	0.50	—	—	7.76	Flakey	—
750.	0.09	0.035	0.24	0.05	—	7.77	Crushed	—
—b	0.43	0.02	0.61	0.03	0.07	—	"	—
—c	—	—	—	—	0.05	—	"	—

From the above results we may draw the following conclusions:—

I. The proportion of oxygen varies from 0 to 0.29 per cent; this latter figure appears to be a maximum—we may therefore agree with Ledebur's observation that 0.29 per cent of oxygen corresponds to the limit of solubility of the suboxide of iron (1.30 per cent) in steel.

II. A steel, to be easily filed, should not contain more than 0.10 per cent of oxygen.

III. The proportion of oxygen present has a distinct connection with the variation in the density.

Thus we see that an easily fileable steel, containing not more than 0.11 per cent of oxygen, has a minimum density of 7.90. A steel containing more than 0.20 per cent of oxygen, and having a density below 7.80, must be looked upon as behaving very badly under the file.

It is curious to note that the samples Nos. 498 and 572, intended for telegraph wires, gave such different results from the point of view of electrical resistance. Sample No. 498, containing 0.15 per cent of oxygen, and having a density of 7.85, had an electric resistance of 11.09 ohms on a wire of 4 m.m. diameter, which fulfils the requirements of the telegraphic department. On the other hand, No. 572, containing 0.29 per cent of oxygen, with a density of 7.72, had a resistance of 11.28 ohms, or 0.19 above the standard. The cause of this difference is to be found in the lower density of the metal, which itself results from the high proportion of oxygen present.

For the closer study of the important part played by oxygen in steel, I undertook a series of estimations of oxygen on the same sample of steel during different phases of its refining. I hoped thus to decide why any given type of steel contained more oxygen than others. At the same time I was enabled to determine the exact part played by ferro-manganese in the refining of steel.

For this purpose I chose sample No. 616. It was made from 2457 kilos. of scrap-steel and 819 kilos. of cast-steel from the Novorossiysk Co. These materials were taken on account of the low proportions of silicon, sulphur, and phosphorus they contained, so that the influence of these elements would not interfere with the experiments in question.

A sample was taken every ten minutes. The two first

were taken from the cold metal, the others at different stages of the refining.

The first addition of ferro-manganese, made after 6 hours 45 minutes, consisted of 12.3 kilos.; the second, after 7 hours 5 minutes, consisted of 24.6 kilos. The original charge was completely melted 5 hours 50 minutes after taking the first sample. The metal was run after 7 hours 15 minutes.

The results of these assays are given in the following table. I have already pointed out that the loss of weight undergone by the filings heated in hydrogen is greater than the weight of water collected, and I attribute this difference to the evolution of the gas dissolved in the metal. I have therefore tabulated this item as well as the proportion of oxygen present.

Sample No. 616.

Time of taking the sample.		Oxygen.	Gas dissolved.	Remarks.
Hrs.	Mins.	Per cent.	Per cent.	
5	50	0'14	0'52	Incompletely melted.
6	00	0'19	0'39	
6	10	0'39	0'65	Completely melted.
6	20	0'34	0'56	
6	30	0'27	0'45	
6	40	0'21	0'35	
6	45	First addition of ferro-manganese.		
6	50	0'05	0'43	
7	0	0'02	0'22	
7	5	Second addition of ferro-manganese.		
7	10	0'00	0'33	
7	20	—	0'11	

In the examination of the results of the estimation of the oxygen, we must first of all state that the two first samples taken cannot be considered as representative of the average composition of the charge. In fact, at the time when these samples were taken, a part of the mass, containing suboxide of iron, still remained on the floor of the furnace unmelted. The sample consisted chiefly of the cast-steel, hence its low proportion of oxygen. We see, further, that when the mass is completely melted (6 hours 10 minutes) the proportion of oxygen immediately becomes much higher (0.39 per cent instead of 0.14 per cent). These two points have been confirmed, not only by analysis, but also by observations made on the state of the charge at different times during the operation.

As soon as the oxygen has obtained its maximum (0.39 per cent), which may be taken as its normal value, its proportion decreases rapidly at the same time as the oxide of iron itself, and that at the expense of the carbon. This gradual diminution continues until the first addition of ferro-manganese. As was to be expected, this addition has the effect of still further deoxidising the bath, and the second addition of ferro-manganese reduces the oxygen present to zero.

The action of the ferro-manganese is well known. The manganese, being more easily oxidised than the iron, takes up oxygen at the expense of the suboxide of iron in the bath, and passes in its turn into the state of oxide which is found in the slag.

If the operation is prolonged after the disappearance of the greater part of the manganese, the proportion of oxygen will be seen to rise again, since the deoxidising elements—manganese and carbon—would be completely eliminated. In this way we can explain the fact that the softer the steel is, and the less reducing agents it contains (manganese, phosphorus, silicon), the more easily it burns. If the ferro-manganese is added too soon, or in too small quantity, it passes into the slag, and the iron—no longer being protected against oxidation—ends by containing a considerable quantity of oxygen.

As for the proportion of dissolved gas, we can see, from the above table, that it diminishes at the same time as the oxygen. At the moment of adding the ferro-manganese it rises rapidly, to again fall in a regular manner. This result was expected; in fact, by the passing of the oxides

into the slag the ferro-manganese encourages the evolution of carbonic oxide, which thus increases the proportion of gas dissolved.

We must also draw attention to the rapid fall in oxygen (0.33 to 0.11 per cent) during the time following the running of the metal. On arriving in the mould the metal contains a high proportion of gas, which is dissolved at a higher temperature, and of which the solubility is less in the cold. This gas is therefore given off rapidly as the temperature of the metal falls. It follows that it is preferable to wait till the boiling which follows the addition of the ferro-manganese is finished, if we wish the casting to be properly made.

To return to the question of the estimation of the oxygen, I have a few remarks to make on the method I was forced to use by reason of not having a better one at my disposal. First we see that the weight of water collected does not correspond exactly with the weight of oxygen contained in the steel. The second figure (gas dissolved) is always higher than the first (oxygen contained).

Further practice in this kind of analysis has shown me that the sulphur and phosphorus contained in the steel form volatile compounds with the hydrogen. This characteristic has already been pointed out by Thidier (*Gorny Journal*, 1883, vi., 458), who worked with moist hydrogen. The phenomenon remains the same, though much less noticeable, with dry hydrogen. Under these conditions it is impossible to control the results obtained by weighing the water.

I now return to a question I have already mentioned. According to Ledebur, carbides of hydrogen are formed when a steel-turning is heated in a current of hydrogen. This author maintains that the formation of these carbides is accounted for by the presence of oil or grease in the steel, coming from the tool used for cutting it (*Stahl und Eisen*, 1882, p. 194).

To verify this point I operated on the three following samples:—

1. Soft steel containing 0.15 per cent of carbon.
2. Hard steel containing 0.43 per cent of carbon.
3. Cast-steel containing 0.48 per cent of combined carbon, 2.90 per cent of graphite.

These three samples were heated for half-an-hour, at a red heat, in a current of pure nitrogen. After cooling in nitrogen, the samples were washed in alcohol and ether, and dried. Calculation then gave the following results:—

1. Soft steel.—0.18 per cent of volatile hydrocarbons; 0.09 per cent of non-volatile hydrocarbons.
2. Hard steel.—0.05 per cent of volatile hydrocarbons; 0.02 per cent of non-volatile hydrocarbons.
3. Cast-steel.—0.05 per cent of volatile hydrocarbons; 0.02 per cent of non-volatile hydrocarbons.

I then heated these same samples, for the same length of time, in a current of hydrogen, and hydrocarbides were still formed; from this we must conclude that these compounds are due to the action of the hydrogen on the carbon in the metal. The following are the results obtained by analysis of the samples:—

For the soft steel, the proportion of carbon fell from 0.15 to 0.11 per cent after heating in hydrogen. For the hard steel, it fell from 0.43 to 0.37 per cent. For the cast-steel the combined carbon had not changed, but the proportion of graphite fell from 2.90 to 2.35 per cent.

These variations are still more marked if we prolong the heating in hydrogen. At the commencement the hydrocarbons form fairly quickly; this action then gradually becomes slower, but it cannot be said that it entirely ceases so long as the metal still retains any carbon. When we remember that carbon forms more or less stable compounds with iron, it is not astonishing that hydrogen, in its turn, forms compounds with carbon more or less rapidly. Of these compounds some are volatile and others non-volatile. In the method proposed by Ledebur the non-volatile hydrocarbides are weighed at the same time as the water; the result, as oxygen, is therefore always too high.

A more exact and rapid method is much to be desired; it would enable us to estimate the oxygen in steel with greater accuracy, and to elucidate in a more definite manner the part played by this element in metallurgical products.—*Stahl und Eisen*, 1899, p. 265.

THE ACTION OF WOOD-CHARCOAL ON THE ORGANIC MATTER IN WATER.

By F. MALMÉJAC.

THREE series of experiments have been carried out.

For the first series we took, by the aid of a pair of pincers, several pieces of wood-charcoal from the centre of a large piece, and carefully blew off all the dust. 20 grms. per litre of this charcoal were placed in water, of which the proportion of organic matter present was known.

For the second series, similar pieces of charcoal from the same lump were carefully washed with boiling distilled water, then placed in the same proportion in a like amount of the same water.

For the third series, the same quantity of charcoal was placed in another equal quantity of the same water, after having been first heated to bright redness.

After a preliminary shaking the water becomes permeated with a very light carbonaceous dust, which requires a very long time to settle, and which should be filtered off before making the estimation of the organic matter. The carbon, heated to redness, also introduces small quantities of ash into the water; this gives the water a milky appearance. Before estimating the organic matter, the suspended particles should be removed by filtering through ordinary filter-paper, previously washed with boiling distilled water.

After four hours' contact, during which the waters were shaken a number of times for an equal period, the organic matter was estimated by Levy's method, and the following results were obtained as a mean of each series of experiments:—

	Organic matter.		Time of contact.
	Alkaline solution.	Acid solution.	
			Hours.
Check sample	3.4	4.6	4
Water treated with unwashed charcoal.. .. .	3.4	5.0	4
Water treated with washed charcoal.. .. .	2.0	3.8	4
Water treated with charcoal heated to redness.. .. .	1.8	3.2	4

The above results are expressed in m.grms. per litre.

1. After four hours the purification by means of unwashed charcoal has not yet commenced; further, this carbon has even introduced a small amount of organic matter into the water, determinable by permanganate in acid solution. This drawback is one that can rarely be avoided when using raw charcoal for the purification of water intended for immediate drinking purposes.

2. The action of the charcoal, washed with boiling distilled water, is shown by a very distinct diminution of the organic matter in the water.

3. The same is the case with the charcoal heated to redness. The purifying power of this last is superior to that of the washed charcoal; after four hours' contact it removes about 50 per cent of the determinable organic matter in alkaline solution, and 33 per cent of that determinable in acid solution.

From these results we may conclude that by the last two methods (washed charcoal, and charcoal heated to redness), we can effect a purification which, with moderately contaminated waters, would give sufficiently good results in a few hours, as far as the organic matter goes. It is advisable not to make use of pieces of charcoal simply freed from surface dust if the water is to be used shortly after treatment.

The action of the charcoal, however, does not stop there; its purifying power continues for a considerable time longer; thus, unwashed charcoal which has no effect after four hours contact, gave on succeeding days a more and more pronounced purification, as shown by the following table:—

Organic matter in m.grms. per litre of water after purification for—

Four hours..	Alkali	3'4
	Acid	5'0
Twenty-four hours	Alkali	2'6
	Acid	3'0
Five days	Alkali	2'0
	Acid	2'2
Eight days	Alkali	2'0
	Acid	2'2
Ten days	Alkali	2'0
	Acid	2'2

These results show that the action of charcoal does not continue indefinitely; according to our experiments its action appears to be limited to five days. We might ask whether there do not exist in the water organic matters non-absorbable by charcoal.

To test this hypothesis, we separated the charcoal which had no further action from the purified water, by passing it through a washed filter, and we added to the water thus obtained a fresh quantity of 20 grms. of charcoal per litre. After five days' contact, with occasional shaking, the organic matter in this water was estimated, and the following results were obtained as the mean of the series:—

Organic matter in m.grms. per litre of water	Alkaline	1'2
	Acid	1'0

After further treatment with charcoal for five days we obtained:—

Organic matter in m.grms. per litre of water	Alkaline	0'8
	Acid	0'6

Finally, a third treatment with charcoal for five days gave the same results.

These experiments show that:—

1. Organic matter, non-absorbable by charcoal, may exist in water.

2. 60 grms. of charcoal, employed successively in 20 grm. doses, does not give three times the purification of the first 20 grms.

It remained to find out whether a double dose of charcoal would give twice as good a result from the point of view of the purification of the water.

For this purpose we made two parallel series of experiments on the same water, using 20 grms. of charcoal per litre for the first and 40 grms. with the second.

When the quantity of charcoal is doubled the purification is not doubled; it would be even of advantage to use successive doses if that did not increase the time required.

Heavy, knotty charcoal absorbs organic matter less rapidly than light smooth charcoal.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xii.

THE IODOMETRIC ESTIMATION OF SUGAR BY MEANS OF FEHLING'S SOLUTION.

By N. SCHVORL.

AFTER Lehmann and Riegler followed Maquenne, who also published a method for the volumetric estimation of sugar by means of Fehling's solution, but it seems to me, contrary to the opinions of these authors, that it is the best to prepare the Fehling's solution according to the old formula of Soxhlet-Meissl; that is to say, containing 5 per cent of soda, and only to take 20 c.c. for each estimation.

Further, the methods described by the above-mentioned authors being vitiated by several errors of more or less im-

portance, I adopted the following modification:—10 c.c. of solution of sulphate of copper (69'28 grms. to 1000 c.c.; 10 c.c.=27'74 c.c. $\text{Na}_2\text{S}_2\text{O}_3$), and 10 c.c. of tartrate solution (346 grms. of Seignette salt and 100 grms. of soda to 1000 c.c.), are run into an Erlenmeyer matras of 200 c.c. capacity; 50 c.c. of distilled water are added, and the whole boiled for two minutes. After cooling the solution under the tap, 10 c.c. of a solution of iodide of potassium at 20 per cent are added, followed by 10 c.c. of sulphuric acid at 25 per cent (1½ vols. of concentrated H_2SO_4 to 8½ vols. of H_2O). The iodine liberated is immediately titrated by means of a decinormal solution of hyposulphite of soda.

Having thus determined the value of the Fehling's solution, we proceed in the same manner with the estimation of the sugar, using such a volume of sugar solution that contains at the most 90 m.grms. of inverted glucose or saccharose, or 125 m.grms. of lactose. The difference between the two titrations represents the quantity of sugar sought for.

When estimating lactose the solution should be kept boiling for five minutes, and it is evident that in this case the boiling must be kept up for the same number of minutes in the determination of the strength of the Fehling's solution.

The following table gives the results obtained with lactose, glucose, saccharose, and starch.

C.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$	Lactose.	Glucose.	Saccharose.	Starch.
1	4'5	3'2	3'1	2'8
2	9'0	6'3	6'2	5'7
3	13'6	9'4	9'3	8'5
4	18'1	12'6	12'4	11'4
5	22'7	15'9	15'6	14'3
6	27'3	19'2	18'8	17'3
7	31'9	22'4	22'0	22'0
8	36'5	25'6	25'2	23'1
9	41'1	28'9	28'4	26'1
10	45'8	32'3	31'7	29'1
11	50'6	35'7	35'0	32'1
12	55'4	39'0	38'3	35'1
13	60'3	42'4	41'6	38'2
14	65'2	45'8	44'9	41'3
15	70'1	49'3	48'2	44'4
16	75'0	52'8	51'6	47'5
17	80'0	56'3	55'1	50'7
18	85'0	59'8	58'7	53'9
19	90'0	63'3	62'3	57'1
20	95'0	66'9	65'9	60'3
21	100'0	70'7	69'6	63'7
22	105'1	74'5	73'3	67'1
23	110'4	78'5	77'1	70'7
24	105'9	82'6	80'9	74'3
25	121'6	86'6	84'7	77'9
26	127'5	90'7	88'6	81'6
27	133'8	94'8	92'5	85'3

—*Zeitschrift für Angewandte Chemie*, vol. xii., p. 633.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 200 samples of water collected by us during the past month, at the several places and on the several days indicated, from the

main of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 200 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month has been remarkably low; rain fell on five days only, viz., the 1st, 26th, 27th, 28th, and 30th; the total being 0.41 inch. The average rainfall for September is 2.43 inches; we thus have a deficit of 2.02 inches, increasing the previous deficit for the year to 2.05 inches, or 11.11 per cent on the thirty years' average.

Our bacteriological examinations of 521 samples have given the results recorded in the following table; we have also examined 34 other samples, from special standpipes, &c., making a total of 555 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	121
New River, filtered (mean of 120 samples) ..	10
Thames, unfiltered (mean of 25 samples) ..	4332
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 284 samples)	14
Ditto ditto highest	180
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	158
River Lea, from the East London Company's clear-water wells (mean of 42 samples) ..	13

Of the 446 samples of filtered water supplied to London, examined bacteriologically during the past month, only nine samples, or 2 per cent of the whole number of samples examined, contained between 100 and 181 microbes per c.c.

The exceptionally small rainfall in the Thames Valley during the month no doubt has contributed largely to maintain the relatively high standard of purity of the London waters for this season of the year.

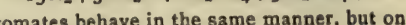
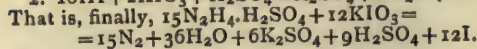
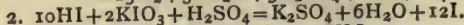
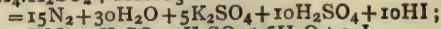
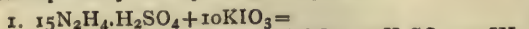
We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

New Method for the Estimation of Hydrazine.—H. Rimini.—If we cause a salt of hydrazone to react on an iodate, an evolution of nitrogen takes place, and at the same time the liquid becomes acid and contains free iodine. The liberated nitrogen or iodine can either of them be estimated, but it is simpler to drive off this latter by boiling, and estimate the remaining iodate. The reaction probably takes place in two phases:—



The bromates behave in the same manner, but only when heated; the chlorates are not decomposed.

The author proposes to extend his examination of this reaction to the estimation of hydroxylamine and semicarbazide.—*Gazz. Chim. Ital.*, (1), vol. xxix, p. 265.

THE SEPARATION AND DETERMINATION OF MERCURY AS MERCUROUS OXALATE.*

By C. A. PETERS.

It is stated in the literature (Rose and Finkener, *Handbuch der Analytischen Chemie*, i., 319) that oxalic acid, neutral and acid oxalates of the alkalis, precipitate mercurous salts, and that oxalic acid and the double oxalates of potassium produce no precipitate with mercuric chloride solution. Starting with these facts, the attempt was made to estimate mercurous salts: volumetrically, by precipitating with ammonium oxalate and determining the oxalic acid by potassium permanganate; and gravimetrically, by direct weighing of the precipitate.

The Volumetric Estimation.

The mercurous nitrate solution used was standardised by the battery, and contained about 12 grms. of metallic mercury to the litre. To obviate the tendency of the mercury salt to break down and form basic salts (Graham Otto, *Handbuch*, iii., 1102) upon the addition of a large amount of water if no nitric acid is added, the solution is prepared in the following manner:—About 20 grms. of mercurous nitrate were ground in a mortar, transferred to a flask, and 200–300 c.m.³ water added. After shaking well, the solution was filtered, and the filtrate diluted to 1 litre. Five c.m.³ of this solution, when precipitated with a sodium chloride solution, gave a filtrate from which only a very slight darkening in colour could be obtained, even upon several hours standing, when treated with hydrogen sulphide, thus showing the absence of a mercuric salt.

A solution made in the above manner had not changed its standard after a period of eight weeks. The potassium permanganate solution (approximately $n/10$) was standardised against lead oxalate.

It was first attempted to estimate the mercurous salts as follows:—The mercurous oxalate was precipitated cold by means of ammonium oxalate, stirred well, and allowed to settle, the completion of the precipitation being determined by addition of more ammonium oxalate. The precipitate was collected on asbestos, washed once or twice with cold water, and (still in the crucible) treated in a beaker with 5 c.m.³ of strong hydrochloric acid. To the solution diluted to 100–200 c.m.³ 1 gm. of a manganous salt was added, and the oxalic acid was titrated with permanganate at the ordinary temperature of the room. The end colour was not stable and was hard to determine. Three experiments, using 0.1217 of mercury in form of mercurous nitrate, gave plus errors of 0.0011 gm., 0.0017 gm., and 0.0028 gm. respectively, or 1.5 per cent. The precipitate when dissolved in sulphuric acid and titrated gave no better results. To obviate this difficulty, the ammonium oxalate solution was matched on the permanganate and the oxalic acid in the filtrate determined. The results obtained by this method, given in the following table, are quite accurate.

Hg taken as $\text{Hg}_2(\text{NO}_3)_2$	Hg found.	Excess of ammo- nium oxalate (sp. gr. approx. 1.16). $n/10$.	HCl (sp. gr. 1.16). $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.	H_2SO_4 (1:1).	Error as Hg.
Grm.	Grm.	C.m. ³ .	C.m. ³ .	Grm.	C.m. ³ .
A.					
1. 0.1825	0.1823	0.90	5	0.5	— 0.0002
2. 0.1217	0.1218	0.93	5	0.5	+ 0.0001
3. 0.1217	0.1206	0.99	5	0.5	— 0.0011
4. 0.1217	0.1210	4.05	5	0.5	— 0.0007
5. 0.3042	0.3034	4.97	5	0.5	— 0.0008
B.					
6. 0.1217	0.1220	0.93	—	—	+ 0.0003
7. 0.1217	0.1211	0.97	—	—	— 0.0006
8. 0.1825	0.1827	0.89	—	—	+ 0.0002
9. 0.3042	0.3040	0.82	—	—	— 0.0002
10. 0.1217	0.1202	4.10	—	—	— 0.0015

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. ix., p. 401.

In the experiments recorded in section A of the table the filtrate was titrated in the presence of hydrochloric acid and a manganous salt, at a temperature of 20–40° (Gooch and Peters, *Amer. Journ. Sci.*, 1899, vii., 461). In the experiments under section B, sulphuric acid was added, and the solution heated in the usual manner. An excess of ammonium oxalate, as shown in experiments 4, 5, and 10, interferes in no way.

The separation of mercurous salt from small quantities of mercuric salts, by the means of dilute nitric acid, sp. gr. 1.15, was next attempted. It is stated (Souhay and Lenssen, *Ann. d. Chem.*, cii., 43) that mercurous oxalate is insoluble in cold dilute nitric acid, while mercuric oxalate is more or less soluble in the same reagent. Before attempting any separation, however, there are three factors with reference to the action of the nitric acid which need to be determined: first, the maximum amount of nitric acid that may be present in titration of an oxalate without interference; second, the maximum amount of nitric acid that may be present in a precipitation of mercurous oxalate without having any perceptible solvent action upon the same; and, third, the amount of mercuric oxalate which will be held in solution by given amounts of nitric acid.

To determine the amount of nitric acid that may be present in the titration of an oxalate, 10 c.m.³ of n/10 ammonium oxalate were titrated with permanganate at a dilution of 100 c.m.³ with sulphuric acid at 80° C. The event proved that 10 c.m.³ of nitric acid, sp. gr. 1.15, may be present without appearance of interfering action. The maximum amount of nitric acid which may be present without action upon the mercurous salt was determined as shown in the following experiments:—

Hg taken as Hg ₂ (NO ₃) ₂ .	Excess of ammonium oxalate (sp. gr. approximately 1.15).	HNO ₃ (sp. gr. at pre-precipitation.	Volume	Hg found.	Error.
Grm.	C.m. ³ .	C.m. ³ .	at pre-precipitation.	Grm.	
0.1122	1.64	10	100	0.1087	–0.0035
0.1122	2.62	6	100	0.1098	–0.0024
0.1122	1.59	6	100	0.1096	–0.0026
0.1122	1.53	5	100	0.1109	–0.0013
0.1122	1.40	5	100	0.1134	+0.0012
0.1122	1.50	5	100	0.1115	–0.0007
0.1122	1.70	4	100	0.1116	–0.0006
0.1122	1.59	8	200	0.1096	–0.0036
0.1122	6.62	8	200	0.1111	–0.0011
0.1122	7.72	8	200	0.1108	–0.0014
0.1122	2.59	5	200	0.1107	–0.0015
0.1010	2.07	5	200	0.1003	–0.0007

Working under the conditions stated in the above table, it is plain that 5 c.m.³ of nitric acid (sp. gr. 1.15) may be used before its solvent action is sufficient to interfere with the accuracy of the process.

To determine the amount of mercuric salt that would be held up by 5 c.m.³ of nitric acid, sp. gr. 1.15, the following experiments were made:—

Hg taken as Hg ₂ (NO ₃) ₂ .	HNO ₃ (sp. gr. 1.15).	Ammonium oxalate (sp. gr. 1.15).	Volume.	Time before precipitation.
Grm.	C.m. ³ .	C.m. ³ .	C.m. ³ .	
0.0335	4	0.75	100	5 hours.
0.0095	4	1.00	100	No precipitate 20 hours.
0.0143	5	6.5	100	"
0.0238	5	1.5	100	Slight precipitate 20 hrs.
0.0238	5	5.5	100	25 minutes.

Five c.m.³ of dilute nitric acid (sp. gr. 1.15) will prevent the precipitation of small amounts of mercuric salt, 10 to 20 m.grms. calculated as mercury, depending upon the amount of ammonium oxalate present in excess. This amount of nitric acid has no apparent solvent action on a precipitate of mercurous oxalate under conditions already

stated, and does not interfere with the titration of an oxalate by permanganate, as already shown.

Carrying out the process of separation of mercurous from mercuric salts, the precipitation was made as described for: the estimation of mercurous salts alone, excepting that nitric acid and mercuric salt were added. The experiments in A, B, and C of the accompanying table show the amounts of mercuric salt from which the mercurous oxalate may be separated with 2 c.m.³ of nitric acid. In experiments in Section A the results are quite accurate, but an excess of ammonium oxalate tends to increase the results a little, as seen in experiments under B. An increase in the amount of mercuric salt present causes also, as shown in Section C, the results to be a trifle high.

Hg taken as Hg ₂ (NO ₃) ₂ .	Hg present as Hg.	Ammonium oxalate (sp. gr. 1.15).	HNO ₃ (sp. gr. 1.15).	Vol. at pre-precipitation.	Hg found.	Error.
Grm.	Grm.	C.m. ³ .	C.m. ³ .	Grm.	Grm.	
A.						
0.1217	0.0067	0.86	2	100	0.1232	–0.0015
0.1217	0.0067	0.92	2	100	0.1220	+0.0003
0.1217	0.0067	0.97	2	100	0.1218	+0.0001
0.1217	0.0067	0.90	2	100	0.1224	+0.0007
0.1217	0.0067	0.91	2	100	0.1213	–0.0004
B.						
0.1221	0.0067	3.92	2	100	0.1237	+0.0016
0.1217	0.0067	3.93	2	100	0.1235	+0.0018
0.1242	0.0067	8.75	2	100	0.1263	+0.0021
C.						
0.1217	0.0134	0.87	2	100	0.1230	+0.0013
0.1217	0.0134	0.86	2	100	0.1232	+0.0015
D.						
0.1217	0.0134	3.93	4	100	0.1218	+0.0001
0.1217	0.0134	3.90	4	100	0.1211	–0.0006
E.						
0.2244	0.0067	1.88	4	115	0.2244	±0.0000
0.2244	0.0067	1.91	4	130	0.2240	–0.0004
EE.						
0.2244	0.0141	2.98	4	100	0.2230	–0.0014
0.2244	0.0141	2.94	4	100	0.2241	–0.0003
F.						
0.2244	0.0067	8.88	4	100	0.2289	+0.0045
0.2244	0.0067	8.90	4	100	0.2285	+0.0041
G.						
0.2424	0.0067	1.75	4	200	0.2432	+0.0008
0.2424	0.0067	2.00	4	200	0.2414	–0.0010
0.2424	0.0067	2.96	4	200	0.2421	–0.0003
H.						
0.2245	0.0134	1.74	4	200	0.2271	+0.0026
0.2245	0.0134	1.81	4	200	0.2256	+0.0012
I.						
0.1122	0.0144	6.62	5	200	0.1121	–0.0001
K.						
0.1122	0.0240	6.54	5	200	0.1136	+0.0014
0.1122	0.0240	6.57	5	200	0.1130	+0.0008

In experiments D, using 4 c.m.³ of nitric acid even in the presence of an excess of ammonium oxalate, the results are accurate. In experiments E the amount of mercurous salt was doubled and the results are accurate. In EE the amount of mercuric salt was also doubled, and the results are still fairly accurate; but when a large excess of ammonium oxalate is present, as in experiments F, even with the smaller amount of mercuric salt, the results are high. At a dilution of 200 c.m.³ the results are normal as seen in experiments G; but the introduction of more mercuric salt, as in experiment H, causes a plus error.

Using 5 c.m.³ of nitric acid, the larger amount of mercuric salt, together with a large excess of ammonium

oxalate, as recorded in experiments K, the error is raised a trifle; but with a smaller amount of mercurous salt as in experiment I the result is normal.

In precipitating mercurous salts by ammonium oxalate ($n/10$) it is an easy matter to keep the excess of the precipitant within the limits of 1 or 2 c.m.³, because the mercurous oxalate, when properly stirred, settled very rapidly.

The Gravimetric Estimation.

All the conditions described above in the volumetric estimation of mercurous oxalate, for the separation of mercurous from mercuric salts, may be applied to the gravimetric estimation of mercurous oxalate. The precipitate is collected on a weighed asbestos filter, washed two or three times with cold water and dried over sulphuric acid to a constant weight. Amounts of mercurous oxalate equivalent to 0.1217 and 0.2244 grm. of metallic mercury dried to a constant weight over sulphuric acid in about fifteen hours; a larger amount equivalent to 0.3 grm. of metallic mercury, required about two days to dry to a constant weight. Souchay and Lenssen (*Ann.*, ciii., 308), state that mercurous oxalate breaks up at 100°; consequently this temperature cannot be used for drying. For example, a precipitate containing 0.1122 grm. mercury as the oxalate which when brought to a constant weight at the ordinary temperature over sulphuric acid weighed 0.1371 grm., and was heated and weighed as follows:—

After 7 hours at 110°, weight = 0.1338 grm.

" 2 " " " 0.1328 "

" 7 " " " 0.1302 "

The result shows a loss of 0.0069 grm. for sixteen hours heating, and agrees with the statement of Souchay and Lenssen.

The following experiments give the results of the gravimetric work, in which the drying was effected, by exposure for fifteen hours or less, at ordinary temperatures, over sulphuric acid. The larger amounts of nitric acid present in the separations cause the precipitate to be more granular and aid in the filtering process:—

Hg taken as $Hg_2(NO_3)_2$. Grm.	Hg present as $Hg(NO_3)_2$. Grm.	Excess ammonium oxalate (sp. gr. 1.15). C.m. ³ .	Volume at precipitation. C.m. ³ .	Hg found. Grm.	Error. Grm.
K.					
0.1217	—	2.4	—	100	0.1217 $\pm$ 0.0000
0.1217	—	2.4	—	100	0.1217 $\pm$ 0.0000
0.1122	—	2.4	—	100	0.1124 $\pm$ 0.0002
L.					
0.1122	0.0067	0.93	2	100	0.1130 $\pm$ 0.0008
0.1122	0.0067	0.93	2	100	0.1112 $-$ 0.0010
M.					
0.1122	0.0067	4.40	2	100	0.1124 $\pm$ 0.0002
N.					
0.1122	0.0135	0.72	4	100	0.1125 $\pm$ 0.0003
O.					
0.2244	0.0071	1.68	4	100	0.2253 $\pm$ 0.0009
0.2244	0.0071	2.46	4	100	0.2241 $-$ 0.0003
P.					
0.2244	0.0048	0.54	4	200	0.2248 $\pm$ 0.0004
0.2244	0.0048	2.44	4	200	0.2245 $\pm$ 0.0001

In Section K are experiments showing the accuracy of the process where a mercurous salt is precipitated in the absence of a mercuric salt. A small amount of mercuric salt was introduced in experiments L, and an excess of ammonium oxalate in experiment M, a still larger amount of mercuric salt was present in experiment N, and a larger amount of mercurous salt in experiments under O. In experiments in Section P a dilution of 200 c.m.³ was employed both with and without an excess of ammonium oxalate. All the results are within reasonable limits of error.

The work may be summed up briefly as follows:—Mercurous nitrate may be estimated volumetrically by precipitating as the oxalate and determining the excess of the precipitant with permanganate.

The precipitated mercurous oxalate may also be estimated gravimetrically by drying it over sulphuric acid and weighing directly.

In solutions containing 2 to 5 per cent dilute nitric acid, sp. gr. 1.15, mercurous salts may be separated quantitatively as the oxalate from small quantities of mercuric salts.

If about 0.12 grm. of mercury is present as the nitrate in 100 c.m.³ of water, about 12 per cent of that amount of mercury as the mercuric salt may be present without interfering with the accuracy of the estimation, and even 20 per cent may be present before an appreciable rise in the result is apparent. If the amount of mercurous salt present is doubled, the amount of mercuric salt which may be present is cut down about one-half.

The author wishes to thank Professor F. A. Gooch for many kind suggestions given during the course of this work.

NOTICES OF BOOKS.

Domestic Science. The Science of Domestic Economy and Hygiene treated Experimentally. By THOMAS CARTWRIGHT, B.A., B.Sc. (Lond.). With numerous illustrations. London, Edinburgh, and New York: Thomas Nelson and Sons. 1900. Pp. 215.

As its title indicates, this book is more particularly suited for girls; indeed, the author insists that girls should be made to carry out all the experiments herein described with their own hands, as they will by this means more firmly grasp the fundamental ideas of domestic economy.

The subjects dealt with are of a very elementary character, and comprise weighing and measuring, the general effects of heat on matter, cooking, the purification and separation of liquids, the transmission of heat with regard to clothing, experiments with coal, candles, and gas-flames, the properties and characteristics of various waters, hard and soft; the preservation of food, &c.; the whole forming a useful and interesting little volume for school-children of both sexes.

Notes on Five Years' Experiments on Hop-manuring, conducted at Golden Green, Hadlow, Tonbridge. By Dr. BERNARD DYER. Reprinted from *The Agricultural Gazette*. London: Vinton and Co. 1900. Pp. 23.

IN this pamphlet Dr. Dyer continues the record of several years' experiments on the manuring of hops, more particularly with the regard to the use of nitrate of soda. On the first page we find the following rather contradictory statements, which we give in the author's own words:—"For many years there has been prevalent among hop-growers an idea that nitrate of soda is an unsafe manure for hops, and likely to injure their quality. On the other hand, the consumption of nitrate of soda in our hop-gardens has, of late, been steadily increasing. Nevertheless, a very large number of hop-growers, while freely using nitrogenous manures of other kinds, fear to make use of nitrate of soda."

From the above statement it would appear that the only explanation of the increased consumption of nitrate of soda would be accounted for by the area under cultivation being increased; this we believe is not the case, but rather the opposite to what has been taking place.

Dr. Dyer's experiments, however, have been carried out with a view to deciding whether or no nitrate of soda has any deleterious effect on the hop crop. It would seem that if nitrate of soda has in some hands proved hurtful, it is because it has been applied without a proper quantity

of phosphates or potash, or because it has been applied too abundantly, or because it has been applied at the wrong time.

The general scheme of the experiments is that on one plot phosphates and potash are applied without any nitrogen, while on five other plots nitrate of soda is added in quantities varying from 2 cwt. up to 10 cwt. per acre, for the most part in successive dressings of 2 cwt. per acre. In the first year the nitrate was not applied till May, while in the succeeding years it was applied earlier, until, in 1899, the first dose was put on early in January.

An examination of the results for this latter year shows that nitrate of soda has proved a valuable addition to the natural resources of the soil, the quantity of hops produced on the nitrated plots being from 2 to 4½ cwt. per acre in excess of the crop produced without artificially applied nitrogen, while the good effect in quality proved to be of even greater importance.

CORRESPONDENCE.

STANDARD OF ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—Acting upon the suggestion of the International Commission on Atomic Weights I offer the following as good reasons for taking oxygen = 16 as the standard:—

1. The atomic weights more nearly approximate whole numbers as they are now given.

2. For student computations and for most practical purposes scarcely half a dozen of the atomic weights need have any decimal at all, the approximate whole number being sufficiently accurate. With hydrogen as the standard twenty differ as much as 0.4 from whole numbers.

3. With oxygen = 16, hydrogen may still be considered as equal to 1, and the decimal may generally be disregarded.

4. For the teaching of chemistry the approximate whole number is desirable, and the accurate weight need be found only in the table.

Let us have only one standard and avoid the present confusion.—I am, &c.,

J. I. D. HINDS.

University of Nashville,
Nashville, Tennessee, U.S.A.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 13, September 24, 1900.

Nature of the Combustible Gases found in the Air of Paris.—Armand Gautier.—The author's former researches on the combustible gases of the atmosphere were performed on pure air, obtained from places free from animal or vegetable contamination. Such a gas contains 19.5 hundred-thousandths of its volume of free hydrogen; this gas is accompanied by mere traces of hydrocarbons. In the air of towns this hydrogen is mixed with other combustible vapours present in sufficient quantity for estimation. The author examined especially the air of Paris, which no doubt is practically the same as that of other industrial and populous towns, and found that the combustible portion of the atmosphere of the streets has the following mean composition, calculated as parts per 100 litres:—Free hydrogen, 19.5 c.c.; marsh gas, 12.1 c.c.; gases very rich in carbon (benzene and its analogues), 1.7 c.c.; oxide of carbon (with traces of hydrocarbons of the series C_2H_{2n} and C_4H_{n+2}), 0.2 c.c.

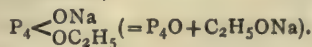
Crystallised Monocalcic Aluminate.—Em. Dufau.—When a mixture of alumina and calcium oxide is heated to a sufficiently high temperature, a combination of the two oxides takes place with formation of monocalcic aluminate, Al_2O_3Ca , crystallised in needle-shaped crystals. This form of crystallisation throws this aluminate out of the group of spinels. It resembles in this manner the aluminate of glucinum, which up to the present time formed the only exception. It may be remarked that calcium chromite, Cr_2O_3Ca , which the author describes in a previous paper, and calcium ferrite, Fe_2O_3Ca , described by J. Percy, also crystallise in needles, and for this reason ought not to be classed as spinels.

MISCELLANEOUS.

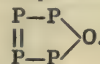
The Lower Oxides of Phosphorus.—A. Michaelis and M. Pitzsch.—A large number of sub-oxides have been described, of which the authors give a detailed history. These compounds contain from 79.49 per cent to 89.08 per cent of phosphorus. They are:—

1. The oxide of Pelouze P_3O
2. The oxide of Le Verrier P_4O
3. The first oxide of Gautier P_4OH
4. The second compound of Gautier .. P_5H_3O
5. The third compound of Gautier .. $P_{13}H_3O_3$
6. The compound of Franke $P_4H(OH)$
7. The oxide of Besson P_2O

The authors have taken up the analysis of these different compounds. To free them from mixed amorphous phosphorus and hydride of phosphorus, they were, after washing with water and the elimination of ordinary phosphorus, dissolved in alcoholic KOH, their only solvent, and reprecipitated with a dilute acid. The authors have distinctly found that only one sub-oxide exists, that of Le Verrier, P_4O . Le Verrier's process is complicated, and the authors have prepared this body by two different methods. The first consists of treating granulated phosphorus, washed with alcohol, with an aqueous alcoholic solution of KHO; hydrogen and a little phosphoretted hydrogen are given off, and a red solution is obtained, from which acids precipitate the sub-oxide according to the equation $P_4 + H_2O = P_4O + H_2$. The second method consists of dehydrating hypophosphorous acid by means of acetic anhydride. The anhydride P_2O being unstable is decomposed according to the equation $2P_2O = P_4O + O$, which oxygen unites with 1 molecule of PO_2H_3 . The precipitate is washed with water and alcohol, then dried in vacuo over P_2O_5 . The sub-oxide P_4O is a fine powder, orange-red, or yellow in colour according to its state of division, with a density of 1.9123 at 26°; it attracts moisture, and gives off an odour of phosphoretted hydrogen; when moist it ignites at 90°, but when dry it can be heated to a much higher temperature. When heated in an inert atmosphere it splits up according to the equation $5P_4O = P_2O_5 + 18P$. Chlorine transforms it into $POCl_3$ and PCl_5 . If it is moistened it gives PO_4H_3 . Warm SO_4H_2 gives PO_4H_3 and H_2S ; NHO_3 inflames it. By its action many metallic solutions are precipitated in the state of phosphide. The alkalis dissolved in aqueous alcohol dissolve it, giving a deep red coloured solution, possibly the alcoholate,—



This red solution gradually loses its colour, giving off hydrogen and phosphoretted hydrogen, and it then consists of PO_2H_3 ; this is formed according to the following equation:— $P_4O + 7H_2O = 4PO_2H_3 + H_2$. The constitution of P_4O may be represented by—



—Lieb. *Annal. Chem.*, vol. cccx., p. 45.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Graphite in Ferro-silicon.—Will some reader kindly inform me of a reliable process for the above.—H. JERVIS, 52, Bannock Street, Sheffield.

MEETINGS FOR THE WEEK.

FRIDAY, 26th.—Physical, 5. Exhibition of Experiments illustrating certain Phenomena of Vision, by Dr. Sheldford Bidwell, F.R.S. "Concentration at the Electrode in a Solution, with special reference to the Liberation of Hydrogen by the Electrolysis of a mixture of Copper Sulphate and Sulphuric Acid," by Dr. J. S. Sand. "Electromotive Force and Osmotic Pressure," by Dr. R. A. Lehfeldt.

TO CORRESPONDENTS.

G. B.—One hundred cubic feet of carbonic acid gas at 0° C. and 760 m.m. pressure requires for its production 25.6 lbs. of whiting (CaCO_3) and 21.6 lbs. of sulphuric acid (H_2SO_4). It would probably be cheaper, and certainly more convenient, to buy carbonic acid ready made in a steel cylinder.

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Further particulars on application to the Director—

ALFRED JØRGENSEN, The Laboratory, Copenhagen, V.

THE CHEMICAL NEWS.

VOL. LXXXII., No. 2135.

THE CONSTITUTION OF CAMPHOR.*

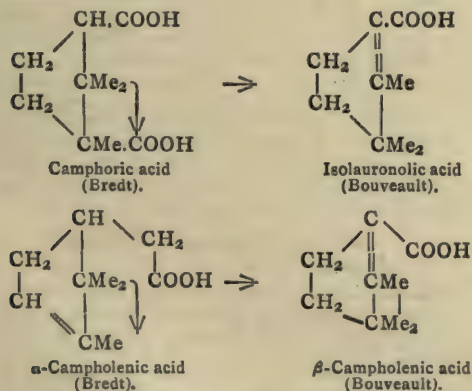
By ARTHUR LAPWORTH, D.Sc.

THE paper deals briefly with the more important facts which have a direct bearing upon the question of the constitution of camphor, and the present position of our knowledge is discussed.

Reasons are given for the view that the Bredt and the Perkin-Bouveault formulæ are the only ones now worthy of consideration, and the evidence in favour of each is reviewed. It is shown that apparently conclusive evidence in favour of either may be brought forward, but that the weight of evidence leans in a marked way towards that of Bredt, the most important obstacles to the final acceptance of that formula being the properties and constitution of the stereoisomeric campholytic and isolaunonic acids and of β -campholenic acid.

The significance of the evidence derived from the study of the β -campholenic derivatives is shown to be materially diminished by the fact that these derivatives are actual products, being produced, probably in all cases, from the α -derivatives, and the properties of the latter are exactly represented by Bredt's formulæ, the inference being that the passage from the one set to the other is the result of an unusual intramolecular change. Moreover, from a consideration of the inactivity and general properties of β -campholenic acid on the one hand and of isolaunonic acid on the other, it would appear that these two substances are very closely related, the former being probably derived from the latter by the substitution of $-\text{CH}_2\text{COOH}$ for $-\text{COOH}$, so that it may be presumed that the internal changes which result in their formation are very similar.

In the author's opinion, the formulæ for isolaunonic acid and β -campholenic acid suggested by Bouveault are almost certainly correct, and it is equally probable that the compounds from which they are obtained are represented by Bredt's formulæ. A comparison of these structures is made, and it is pointed out that the essential structural change appears in each case to be the migration of a single methyl group from one carbon atom to another immediately adjacent.



Some assumption of this kind would certainly appear to be necessary, and the one here advanced is probably the simplest possible. The migration of methyl groups from one carbon atom to another is not infrequent, and to

* Abstract of a Paper read before the British Association (Section B), Bradford Meeting, 1900.

recall the readiness with which pinacone is converted into pinacolone is to perceive the possibility of a transference of methyl in the case here considered. It is specially significant, too, that when a methyl group migrates in the molecule of a hexamethylene compound during conversion into a benzenoid derivative, it is the adjacent carbon atom to which it is transferred.

The properties of *w*-bromocamphoric anhydride and camphanic acid are discussed in connection with the question of the relationship of camphoric acid to succinic and glutaric acid, and reference is also made to the properties of Noyes's hydroxydihydrolauronic acid, which are not in accordance with the requirements of Bredt's formula for camphor.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART IV.

NICKEL AND COBALT.

By HARRY BREARLEY.

(Continued from p. 187).

COBALT.

I. SEPARATING FROM NICKEL.

I. 1. Depending on Behaviour with KCN.—

598. GIBBS (C. N., xi., 125).—By using a solution of HgO in KCN to precipitate Ni from the double cyanide of Ni and Co, the separation is immediate and complete; the precipitates may be ignited and weighed at once; Co determined by difference. Separation with KNO_3 lengthy and difficult.
599. HADOW (C. N., ii., 86).—In Liebig's process KCN should be added *before* the KHO; SiO_2 should be absent. Precipitation of the Ni by Cl or a salt of Hg preferable to HgO. If cobalt is finally precipitated with HgNO_3 (Wöhler's process), chlorides and sulphates should be absent.
600. FLECK (C. N., xiii., 299).— NH_3 solution exposed to air, $(\text{NH}_4)_2\text{S}$ added, NH_3 evaporated, and KCN added; the nickel sulphide dissolves.
601. GUYARD (C. N., xxxiv., 255).—Precipitate as sulphides, dissolve out Ni with KCN, acidulate filtrate, and ignite precipitated nickel cyanide to oxide.
602. JORISSEN (C. N., xlv., 240).—Precipitate with NaHO and Br, and dissolve out Ni with KCN; not good for much Ni and little Co.

I. 2. Depending on Behaviour of Oxidised Compounds.—

603. FLEISCHER (C. N., xxii., 96).—Add hypochlorite and KHO, boil until precipitate is black, then dissolve out Ni_2O_3 with $(\text{NH}_4)\text{HO}$.
604. DONATH (C. N., xlvii., 248).—Halve the solution; precipitate both metals as sesquioxides in one, and Co alone with KHO and I in the other; distil each precipitate with HCl and estimate the Cl with KI and hyposulphite.
605. DELVAUX (C. N., xliii., 196).—Dissolve oxides or sulphides in aqua regia, add $(\text{NH}_4)\text{HO}$ and permanganate, then KHO to precipitate the Ni. The precipitate must be separated from Mn.
606. VORTMANN (C. N., xlix., 150).—Uses hypochlorite instead of permanganate (605); detects traces of either metal in the other. (See also 510).
607. McCULLOCH (C. N., lvi., 27).—Examination of Fleischer (603) and Donath (604) processes. The Co is not oxidised to Co_2O_3 . Nickel salts precipitated with NaHO and an oxidising reagent varied from Ni_2O_7 to Ni_3O_4 .
608. BAYLEY (C. N., xxxix., 81).—Ni and Co are not oxidised by hypochlorite to Ni_2O_3 , but to Ni_3O_5 and Co_3O_5 , which are further decomposed on boiling.

609. ARNOLD ("Steel Works Analysis," p. 166).—By precipitating with Br and NaHO, the compound formed contained only about 15 per cent Ni_2O_3 .
610. CARNOT (C. N., lix., 183).—Co precipitated by H_2O_2 and KHO is exactly Co_2O_3 ; precipitated by hypochlorite, Br, or I, the proportion of O is greater; under the latter conditions, the Ni is exactly Ni_2O_3 . Estimation and separation of the metals based on these facts. McCulloch (C. N., lix., 205) disputes the fundamental facts, and (C. N., lix., 208) makes unsuccessful attempts to separate the metals after oxidation in ammoniacal solution.
611. FISCHER (Z. C. S., lvi., 653).—Alkaline solution boiled with H_2O_2 , and the oxygen in the Co_2O_3 estimated with KI and $\text{Na}_2\text{S}_2\text{O}_3$.
612. CARNOT (C. N., lx., 54).—To acid solution add $(\text{NH}_4)\text{HO}$ and H_2O_2 ; or precipitate ammonio-cobalt molybdate from acetic solution with $(\text{NH}_4)_2\text{MoO}_4$; Ni in solution; Zn and Cu do not interfere. A good way of detecting cobalt.
613. TERREIL (C. N., xliii., 133).— KMnO_4 added to hot ammoniacal solution, and then a faint excess of HCl; after a time, roseo-cobaltic hydrochlorate is precipitated. Detects 0.01 per cent Co in Ni.
- I. 3. Separation as Phosphate.—
614. DIRVELL (C. N., xl., 268).—Co precipitated by microcosmic salt and ammonium acetate as $\text{NH}_4\text{O}_2\text{CoO}_2\text{PO}_5 + 2\text{H}_2\text{O}$ and ignited to pyrophosphate. The method is rapid.
615. HOPE (Z. S. C. I., 1890, 375).—Uses this process with electro-estimation for analysis of ores, mattes, &c.
616. CLARKE (C. N., xlviii., 262).—A careful examination of Dirvell's process. Accurate results with any proportion of Co and Ni. Process considerably modified.
617. CLARKE (Z. S. C. I., 1896, 867).—Dirvell's process does not precipitate Co if present as cobaltic salt, and therefore by means of Br and H_2O_2 , and the process (575) Ni is precipitated in the presence of Co.
- I. 4. Miscellaneous Processes for Separating Ni and Co.—
618. FLEITMANN (C. N., xxxii., 260).— KNO_2 fails to separate 1 per cent Co from Ni. The Co is precipitated along with a little Ni by means of hypochlorite, and then the nitrite separation of the Co made.
619. BAUBIGNY (C. N., lxi., 224).—Ba, Ca, Sr, and Pb interfere with the nitrite separation. KNO_2 should always be tested for Pb.
620. ILINSKI and KNORRE (C. N., li., 170).—Precipitate cobalt with nitroso- β -naphthol, ignite with oxalic acid, and reduce to metal; Fe and Cr must be absent (see 25 and 26).
- C. N., liii., 301.—Cobalt-nitroso- β -naphthol is permanent in the presence of acids, alkalis, and oxidising and reducing agents; stability with various reagents, and means of preparing the nitroso- β -naphthol given.
621. KNORRE (Z. C. S., xlviii., 840; and lxi., ii., 500).—Scheme for analysis of commercial Ni; separation as above; cobalt ignited to Co_3O_4 .
622. PHIPSON (C. N., xxxii., 150).—Co and Ni are precipitated together by potassium xanthate; on making slightly ammoniacal, the Ni passes into solution.
623. HAVENS (C. N., lxxviii., 323).—Pinerva's process (512) does not effect a complete separation. Part of the cobalt, if present in considerable amount, goes down with the Ni.
624. GUCCI (Z. C. S., l., 1077).—Mixed sulphides are fused with KNO_3 ; from the oxides, undissolved by water leaching, Ni is completely dissolved by 1.20 HNO_3 .
625. BAUBIGNY (C. N., lvii., 55).— H_2S does not precipitate all the Co before acting on the Ni, in an acetic solution, as has been stated, and therefore no process on these lines is quantitatively available. (See 561).
626. CLARKE (C. N., xx., 154).—Metals precipitated with ferricyanide from a $(\text{NH}_4)\text{Cl}$ solution; nickel dissolved from precipitate with $(\text{NH}_4)\text{HO}$; cobalt absolutely insoluble; process given as qualitative.
627. HERRENSCHMIDT (C. N., lxi., 112, &c.).—Cyanide superior to nitrite method of separation. Traces of Ni can be microscopically detected in cobalt hydroxide; weigh Ni and Co together as sulphates; determine Ni separately as sulphate after separating with KCN, Br, and Cl; Co by difference. Discusses (p. 128) Baubigny's separation of Zn (534); review experiments on the state of oxidation when Ni and Co are treated with oxidants in alkaline solution. Carbon monoxide (Mond's process) is recommended for the absolute separation of Ni and Co.
628. KRAUSS (C. N., lxxiii., 254, &c.).—An examination of fourteen methods founded on the different behaviour of the higher oxides of the metals; two depending on the behaviour of the sulphides, Dirvell's process (614) and Clarke's modification of it (616); and six methods based on various principles. This memoir practically covers the whole ground up to 1891.
- II. SEPARATION OF COBALT FROM OTHER ELEMENTS.
629. Zinc.—VORTMANN (Z. C. S., lxxviii., ii., 89).—Electro-deposition of Co from alkaline tartrate solution.
630. WALLER (Z. S. C. I., 1897, 1043).—A summary of proposed means of making the electro-separation. (See also 524, 528, &c.).
631. Bismuth.—JANNASCH and KAMMERER (C. N., lxxii., 91).—On pouring a nitric acid solution of the metals into ammoniacal H_2O_2 Bi is precipitated.
- III. GRAVIMETRIC ESTIMATION OF COBALT.
632. GIBBS (C. N., xvii., 172).—Neutral solution boiled with soda acetate and hypochlorite. The Co_2O_3 , reduced to Co in H, is free from alkali; Ni may be similarly estimated; this is Popp's process.
- 632a. GIBBS (C. N., xxviii., 51).—Co converted to cobalticyanide, precipitated with HgNO_3 and HgO , ignited in air, and then reduced to metal in H.
633. RUSSELL (C. N., vii., 43).—Ignition in a powerful blast blowpipe and cooling in a current of CO_2 forms true protoxide of cobalt.
634. SALVETAT (C. N., x., 91).—Oxide is calcined with a salt of Al, leaving a known residue. The increase in weight represents protoxide of cobalt.
635. FRESSENIUS (C. N., iv., 150).— $(\text{NH}_4)_2\text{S}$ does not precipitate dilute Co solutions; NH_4Cl assists, $(\text{NH}_4)\text{HO}$ slightly retards, precipitation.
636. MOORE (C. N., lxi., 75).—Decompose Mn ores by fusion; precipitate Ni and Co as sulphides, convert to sulphates, and electro-deposit; separate Co by precipitation as ammoniac phosphate. A rapid process is based on the absorption of oxygen by ammoniacal solutions of cobalt according to the equation $2\text{CoO} + \text{O} = \text{Co}_2\text{O}_3$.
- IV. VOLUMETRIC ESTIMATION OF COBALT.
- IV. 1. Oxidimetric Processes.—
637. WINKLER (C. N., x., 215).—Co may be estimated in presence of Ni by precipitating with HgO and a standard solution of KMnO_4 ; recognises 0.1 per cent Co in Ni; oxygen compounds of Cl, S, As, and P interfere; As and P eliminated by adding Fe_2Cl_6 and precipitating with HgO .
638. DONATH (C. N., xli., 15).—Modified Fleischer's process (603). In one portion converts to Co_2O_3 and Ni_2O_3 with bromine, and in another to Co_2O_3 and NiO with KHO and boiling. Each precipitate is distilled with HCl.
639. McCULLOCH (C. N., lix., 51).—Measures the oxygen necessary to convert cobalto- to cobalticyanide;

- the operation is performed in absence of air- and at barometric pressure. Ni, Mn, Pb, P, As, Al, Zn, Sb, Mo, and U do not interfere; Cu and Fe do.
640. MOORE (C. N., lxxviii., 295).—The change from cobalto- to cobalti-cyanide either in alkaline or acid solutions is accompanied by greater absorption of O than is expressed by the usual equation, $2K_4CoCy_6 + H_2O + O = K_6Co_2Cy_{12} + 2KHO + H_2O$.
641. JOB (C. N., lxxviii., 254).—Alkaline cobalt solutions peroxidised with H_2O_2 , and the Co_2O_3 formed titrated with a ferrous solution.
642. KARSLAKE (Z. C. S., lxiv., ii., 194).—Precipitate as cobaltinitrite, boil with KHO, and titrate with permanganate; the oxidation is from the nitrous acid of the $K_3Co(NO_2)_6$ to nitric acid.
643. JOLLES (Z. C. S., lvi., 798).—The cobaltous solution is run into a measured volume of manganate until the latter is decolorised; $CoMnO_3$ is precipitated.
644. REIS and WIGGERT (Z. C. S., lx., 620).—Oxidation to cobaltic oxide with permanganate in presence of ZnO; excess of $KMnO_4$ titrated with arsenious acid.
645. PURGOTTI (Z. C. S., lxxii., ii., 77).—After converting to the sesquioxides, either Ni or Co may be estimated by titrating with a solution of the blue oxide of molybdenum (Mo_3O_8). (See also C. N., xxxviii., 22).
646. ROSSLER (C. N., xli., 184).—Cobaltous solution mixed with standard silver and KHO solution; $Ag_4OCo_2O_3$ is precipitated. Proceed thence as for Mn (207). Ni causes low results.
- IV. 2. Miscellaneous Processes.—
647. NEUMANN (Z. C. S., lxxviii., ii., 64).—Either Ni or Co estimated by titration with soda sulphide.
648. KRIEDER (Z. C. S., lxxviii., ii., 534).—The HCl solution of the ore precipitated with chalk, and a fraction of the filtrate colorimetrically compared with standard cobaltous chloride solution.
649. BREARLEY (C. N., lxxvi., 165).—Cyanometric estimation, using the AgI indicator as for Ni (581).
650. HARRIS (Z. C. S., lxiv., ii., 487).—A criticism of Winkler's (637), McCulloch's (639), Fleischer's (603), Donath's (638), and von Reis's methods. None of them quite satisfactory.
- V. DETECTION OF COBALT.
651. BRAUN (C. N., xii., 58).— KNO_2 and acetic acid added to a solution of Co in KCN gives a deep red solution.
652. SKEY (C. N., xv., III).—In an ammoniacal solution in tartaric or citric acid ferricyanide produces a dark red colour. Can detect one part in 400,000. C. N., xv., 328.—Any other acid may be substituted for tartaric (see 588).
653. REICHEL (C. N., xliiii., 7).—The KHO precipitate of the Ni and Co is heated with KHO (solid) and a little H_2O . The Co dissolves with a blue colour, and may be precipitated from the filtrate with ether.
654. TATTERSALL (C. N., xxxix., 66).—Add KCN and yellow $(NH_4)_2S$; blood red = Co; only Cu interferes. Papasogli (C. N., xxxix., 149) says this test is most sensitive when the $(NH_4)_2S$ is superstratified.
655. PAPASOGLI (C. N., xli., 74).—The previous reaction and a red colour formed when Zn is added to the double Ni and K cyanide are used to detect the one metal in the presence of the other.
656. PAPASOGLI (Z. S. C. I., 1899, 74).—Saccharose and soda give a violet colour with one part Co in 50,000; further tests with amylsulphocarbonate, &c., are applied when Ni is also present.
657. MOORE (C. N., lxxviii., 295; and lxxi., 81).—Investigates the cause of the red colour used by Papasogli (655) as a test for Ni.
658. BALL (C. N., lxx., 36).—Pour a little of the solution on to anhydrous thiosulphate and heat; green colour = Co. Ni, Fe, Mn, &c., do not interfere.
659. DURRANT (C. N., lxxiii., 228).— $Na_2CO_3 + H_2O_2$ give a green liquid with Co in presence of much Ni.
660. COEHN (Z. S. C. I., 1898, 605).—Co is detected in presence of Ni by its deposition in the fine cracks of a glass tube (stenolysis).
661. VON ILINSKI (Z. C. S., lxx., ii., 451).—Add fresh nitroso-β-naphthol to HCl solution; dark red precipitate = Co. Works well in the presence of Ni.
662. WOLFF (C. N., lxvii., 94).—Fe precipitated from solution of the sulphocyanides with Na_2CO_3 . Shake the filtrate with amyl alcohol and ether; cobalt is distinguished with the spectroscope by the absorption band between C and D.
663. BETTINK (Z. S. C. I., 1899, 519).—To detect Co in Fe treat the solution with KCNS and $Na_2S_2O_3$ until the red colour disappears, filter, and add alcohol-ether; a blue colour indicates Co.
664. JAWOROWSKI (Z. C. S., lxxv., 61).—Add soda pyrophosphate to neutral solution, dilute till solution is colourless, add Na_2CO_3 and Br; a reflected green colour indicates cobalt.

PREPARATION AND PROPERTIES OF THE SO-CALLED "NITROGEN IODIDE."

By F. D. CHATTAWAY and K. J. P. ORTON.

NITROGEN iodide was originally obtained by Courtois (*Ann. Chim.*, lxxxviii., 304) in 1813 by the direct action of ammonia on solid iodine. Solutions of iodine in alcohol, chloroform, carbon tetrachloride, or aqueous potassium iodide, were substituted for solid iodine by later observers, and both alcoholic and aqueous solutions of ammonia have been employed. In all cases a black or dark brown amorphous solution was obtained.

Sérullas (*Ann. Chim. Phys.*, 1825 [2], xxii., 172; and 1829, xlii., 200) prepared the substance by the interaction of iodine monochloride and a solution of ammonia, a method which was afterwards employed by Bunsen (*Liebig's Ann. Chem.*, 1852, lxxxiv., 1). We have prepared nitrogen iodide by these various methods, and have compared the products, which we find to be identical when proper precautions are taken to ensure the removal of all free iodine and ammonia and to prevent decomposition.

Whenever iodine itself is used, whether in solution or as a solid, less than half appears as nitrogen iodide. Exact experiment showed that at ordinary laboratory temperatures the nitrogen iodide formed contains about 47·5 per cent of the iodine used. Of the remainder, 51·6 per cent appears as ammonium iodide and 0·8 per cent as ammonium iodate.

The use of alcoholic solutions of iodine or ammonia decreases largely the yield, because the nitrogen iodide reacts rapidly with the alcohol to form iodoform, which, moreover, can never be wholly removed from the product. Bunsen, however, used this method and obtained a substance, analysis of which led him to the formula $N_2H_5I_3$ for nitrogen iodide. All our analyses of nitrogen iodide prepared in various ways agree absolutely with this formula.*

Preparation of Nitrogen Iodide by the Action of Iodine Monochloride on a Solution of Ammonia.

When iodine monochloride is used 95 per cent of the iodine appears as nitrogen iodide. The remainder is converted into ammonium iodide and iodate, while the chlorine appears as ammonium chloride. We have carefully investigated this method, and consider it the most

* Bunsen determines the relation of nitrogen to iodine only, and in his method of analysis any trace of iodoform present would not cause error.

suitable for preparing pure nitrogen iodide in large quantities. The best procedure for the preparation of the iodine monochloride and of the nitrogen iodide is as follows:—

One hundred grms. of finely powdered iodine are placed in 300 c.c. of hydrochloric acid of sp. gr. 1.15 in a porcelain basin, and 28 c.c. of nitric acid of sp. gr. 1.41 are added. This quantity of nitric acid provides just sufficient chlorine to convert the iodine into iodine monochloride. The mixture is warmed on a water-bath to about 40°, and continuously stirred, the beginning of the reaction being marked by the colour of the liquid changing from brown to pale yellow. The iodine gradually dissolves, and the solution becomes orange in colour. If the mixture be well stirred, and the temperature not allowed to rise above 40°, no chlorine escapes. After the whole of the iodine has dissolved, the water in the bath is boiled for some time in order to expel the nitrosyl chloride. With the excess of hydrochloric acid used, the solution of iodine monochloride is perfectly stable and undergoes no decomposition even when boiled. To prepare nitrogen iodide it is cooled and diluted by adding about three times its bulk of crushed ice.

For every 10 grms. of iodine 100 c.c. of strong commercial ammonia (sp. gr. 0.880) are poured over about three times their weight of crushed ice, and the cold solution of iodine monochloride slowly run in, the mixture being vigorously stirred during the addition.* The black precipitate of nitrogen iodide which at once separates is filtered off by a pump through asbestos and washed with dilute ammonia, and finally, if required free from ammonia, three or four times with water. In this way a kilogram. of nitrogen iodide can be obtained as a compact cake with perfect safety. It is best, if possible, to leave the solid mass damp with strong ammonia, for then filter-paper can be used instead of asbestos, and the slight decompositions which take place in the total absence of ammonia, and may give rise to local explosions, is prevented.†

Preparation of Crystalline Nitrogen Iodide.

In the course of this investigation it became obvious that nitrogen iodide is not formed by a direct substitution of iodine for hydrogen in ammonia, but that the iodine reacts with ammonium hydroxide, as with other alkalis, to form ammonium iodide and hypoiodite, and that the latter then decomposes, forming nitrogen iodide. This view was originally offered by Schönbein (*Journ. Prakt. Chem.*, 1861, lxxiv., 385) as a suggestion, which has been endorsed by Seliwanow (*Ber. d. Chem. Ges.*, 1894, xxvii., 1012). The addition of ammonia to an alkaline solution of potassium hypoiodite should, therefore, lead to the formation of NH_4OI , ammonium hypoiodite, which should then decompose, producing nitrogen iodide. This we have found to be the case; and, further, under certain conditions of concentration the nitrogen iodide separates in a crystalline form.

The following method gives good results:—A decinormal solution of iodine monochloride is prepared by diluting with water to 1 litre a solution of iodine monochloride, ICl , made as above, from 12.7 grms. of iodine. This dilute solution is unstable, and should only be prepared immediately before use. Fifteen c.c. of this solution are added to 100 c.c. of a half-normal solution of potassium hydroxide (3 per cent), and then, as rapidly as possible, 10 c.c. of ammonia (sp. gr. 0.880) are run in while the solution is gently shaken. The pale yellow liquid remains clear for a short time, but within a minute glittering copper-coloured crystals of nitrogen iodide begin to sepa-

rate, and after a few minutes the crystallisation is complete. The yield is satisfactory, being from 65 to 70 grms. per 100 grms. of iodine. When larger quantities than those indicated are used the yield is not so good, owing to the difficulty of mixing the solutions sufficiently rapidly. Under the microscope very minute needles first become visible, which steadily grow to the usual crystals. The large excess of potassium hydroxide used prevents any setting free of iodine when the acid solution of iodine monochloride is added to it. If more than 15 c.c. of ICl is added to 100 c.c. $\text{KOH}/2$, the crystals separate more rapidly and are smaller. With further increased concentration the crystals become mixed with amorphous nitrogen iodide, which finally forms the chief product.

Replacement of ammonia by a dilute solution of an ammonium salt also causes a deposition of crystalline nitrogen iodide, if the ammonium salt be added very cautiously. An amorphous precipitate is obtained if the solution of ammonium salt be added rapidly, or if it be concentrated.

Amorphous nitrogen iodide can be converted into the crystalline variety by an apparent re-crystallisation from a hot solution of ammonia. The conversion is, however, really due to the occurrence of a reversible reaction in the system (nitrogen iodide + ammonium hypoiodite + ammonium hydroxide). In this system, at the state of equilibrium, the concentration of ammonium hypoiodite is greater at a high than at a low temperature with a given concentration of ammonia. To obtain crystalline nitrogen iodide by this method about 0.5 gm. of the amorphous substance is heated with 100 c.c. of thrice-normal ammonia solution, in which it partially dissolves, producing a pale yellow solution, and this, after filtration through asbestos, deposits crystals when rapidly cooled. With larger quantities the time required to cool the bulk of hot liquid leads to the conversion of so large a proportion of the ammonium hypoiodite into iodate and iodide that little nitrogen iodide separates.

Crystals can also be obtained by the direct addition of a solution of iodine monochloride to ammonia. For this purpose the solution of ICl must be about one-fiftieth normal, and must be added very slowly to a fairly concentrated solution of ammonia.*

Properties of Nitrogen Iodide.

Crystals of nitrogen iodide suspended in water look like splinters of burnished copper, and when dry have a ruby-red colour and a fine lustre. Ordinary amorphous nitrogen iodide shows no trace of crystalline structure, and appears quite black when suspended in water, but if filtered off and dried is seen somewhat to resemble the crystalline substance in colour.

Pure nitrogen iodide is without effect on a neutral solution of litmus, and gives no reaction of iodine when shaken with chloroform. In contact with water it soon shows signs of decomposition, the amorphous more rapidly than the crystalline variety. The crystals lose their lustre, and under the microscope are seen to be etched and corroded. Too prolonged washing with water on the filter will cause this decomposition to take place. Free iodine is then always found by the chloroform test in the solid residue, while free ammonia can be detected in the filtrate.†

Nitrogen iodide can be dried over lime or baryta in an

* The formation of nitrogen iodide has been observed in the action of bleaching-powder on a solution of ammonium iodide.—(Playfair in discussion on Gladstone's paper, *Chem. Soc. Journ.*, 1852, iv., 34). In this case undoubtedly ammonium hypoiodite is first produced, and from it the nitrogen iodide is formed. The product separating is always mixed with calcium iodate, which can only with difficulty be removed by prolonged washing with ammonia. In the electrolysis of an ammoniacal solution of potassium iodide, Losanitsch and Jowitschitsch (*Ber. d. Chem. Ges.*, xxix., 2430) noticed that at the positive pole nitrogen iodide was deposited, and that hypoiodite could be recognised in the solution.

† Pure nitrogen iodide consequently cannot be obtained, as many observers have stated, by washing the product until the filtrate becomes neutral.

* The solution of ammonia should not be added to the solution of iodine monochloride, for then iodine is liberated and the yield much reduced.

† André (*Journ. Pharm.*, 1836, xxii., 137) obtained nitrogen iodide by the addition of ammonia to a solution of iodic acid in hydrochloric acid. Such a solution contains iodine monochloride after it has been heated, for, as is well known, iodic and hydrochloric acids then react according to the equation $\text{HIO}_3 + 5\text{HCl} = \text{ICl} + 2\text{Cl}_2 + 3\text{H}_2\text{O}$.

atmosphere of ammonia, if light be absolutely excluded, without any decomposition taking place. When dry it can be safely detached from a porous tile with a spatula, but slight percussion, pressure between hard surfaces, or rapid heating cause it to detonate with violence. The whole mass explodes at once without scattering, but the explosion is never communicated to any of the substance lying only a few centimetres away. A puff of violet vapour surrounded by a cloud of white fumes is seen, and in a dark room a green flash of light is noticed, resembling in colour the flame of burning ammonia. Nitrogen iodide is remarkably sensitive to light. Bubbles of nitrogen are slowly given off in diffused light from the compound suspended in water, while in direct sunlight rapid effervescence takes place. The dry substance in diffused light becomes gradually covered with minute crystals of iodine, which appear more quickly and grow more rapidly in sunlight.

Partially decomposed nitrogen iodide is very unstable and explodes at the slightest touch.

The following description of the crystals of nitrogen iodide has been given us by Mr. W. J. Pope, who very kindly undertook their examination:—The crystals are small, flattened needles, of a bright ruby colour in transmitted light. The extinction through all faces in the zone of the long edge is straight, and the crystals are probably orthorhombic; the forms would then be $\{001\}$, $\{101\}$ and $\{110\}$ and the crystals are lengthened in the direction of the axis b . The plane angle between the edges $001 : 101$ and $001 : 110$ is 140° , and very frequently only one face of $\{110\}$ is present at one end. An optic axis can be sometimes just discerned at the edge of the field, emerging in the plane $\{010\}$.

The crystals are dichroic. On looking through $\{001\}$ using light polarised in the plane $\{100\}$, light of a beetle-green colour is transmitted, but if the plane of polarisation be $\{010\}$ light of a ruby-red colour comes through.

The specific gravity of crystalline nitrogen iodide is about 3.5. This number has been obtained by drying a quantity of the substance in an atmosphere of ammonia in a specific gravity bottle, and weighing it first in air and then under water.—*American Chemical Journal*, xxiii., No. 5.

THE PREPARATION OF PURE TELLURIUM.*

By JAMES F. NORRIS, HENRY FAY, and D. W. EDGERLY.

In testing a volumetric method (*Amer. Chem. Journ.*, xx., 278), for the estimation of tellurium which we proposed some time ago, we were led to study the methods which had been used for the purification of tellurium. As it appeared that a substance of undoubted purity could be obtained only by a very long series of operations, which involved fusion with potassium cyanide, precipitation, and subsequent distillation in hydrogen, a new method was sought. It seemed probable that the basic nitrate of tellurium might be used for this purpose, as it is a well-crystallised compound, very easily obtained. We accordingly prepared it, and having found that the sample did not agree in some of its properties with those which had been assigned to it in the literature, a careful study of it was made. Klein and Morel (*Bull. Soc. Chim.*, [2], xliii., 198), prepared the compound by dissolving tellurium in nitric acid (1.25 sp. gr.) and evaporating the solution. To the crystals which formed they assigned the formula $4\text{TeO}_2 \cdot \text{N}_2\text{O}_5 \cdot 1\frac{1}{2}\text{H}_2\text{O}$. Only very small crystals were

formed and these were hygroscopic. The nitrate prepared by us by the method of Klein and Morel was obtained in crystals sometimes a centimetre in length and were not hygroscopic. An analysis was accordingly made, which showed that the compound has the formula $4\text{TeO}_2 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$, or better $\text{Te}_2\text{O}_3(\text{OH})\text{NO}_3$, since the water is not present as water of crystallisation.

In the preparation of the nitrate it is crystallised from nitric acid, and as the impurities present in the tellurium do not form crystalline compounds under these conditions, it was thought that the salt could be obtained quite pure. The tellurium obtained from it would, as a result, be free from those substances with which it is invariably mixed when precipitated from solution by sulphur dioxide or other reducing agents. A sample of basic nitrate was recrystallised three times and then subjected to a careful study, with the result that no impurity was discovered.

On account of the fact that the most trustworthy atomic weight determinations of tellurium have given results which place it in the eighth group in the periodic system of the elements, notwithstanding its striking similarity to sulphur and selenium, the hypothesis has been put forward that tellurium is a mixture of true tellurium with an atomic weight of about 125, and another element with a higher atomic weight. Brauner (*Journ. Chem. Soc.*, lxx., 382; and lxxii., 549), who spent a number of years studying tellurium, has expressed this as his opinion.

As no known substance was found in the tellurium obtained from the pure nitrate, the element was subjected to a fractionation to determine whether it could be broken down into two or more substances by this means, which proved so effective in the case of didymium. The double bromide of tellurium and potassium made from tellurium dioxide, hydrobromic acid, and potassium bromide prepared with the greatest care, was carried through a fractionation which involved over 200 crystallisations. In order to determine whether this fractionation had accomplished any decomposition, the tellurium from the end fractions was converted into the nitrate, and the loss in weight of the latter compound on ignition determined. Any change in atomic weight could be determined in this way. The results obtained with the two fractions were identical within the limits of accuracy of the method. The differences obtained, 0.4 of a unit in the atomic weight, was probably due to inaccuracies in the method. The conversion of the nitrate into the oxide, as at present carried out, does not appear to give results from which the atomic weight of tellurium can be determined with great accuracy.

Preparation of Basic Tellurium Nitrate.

The tellurium used was obtained from a residue obtained in the electrolytic refining of copper. This residue was a solution which consisted principally of the sodium salts of tellurous, selenous, and silicic acids, with the last-named acid in great excess. Whitehead (*Journ. Amer. Chem. Soc.*, xvii., 849), has described the process by which the copper is refined, and how the liquid is obtained. Tellurium was obtained from this liquid in two ways. At first the solution was diluted with water, and neutralised with sulphuric acid, which threw out a heavy white precipitate of tellurous acid and silica. This mixture was evaporated to dryness twice with hydrochloric acid to render the silica insoluble, and the residue extracted several times with strong hydrochloric acid. From the solution of the chloride so formed, the tellurium was obtained by precipitation with acid sodium sulphite. In later experiments the tellurium was precipitated from the hot alkaline solution with commercial glucose. The tellurium obtained by both methods contained silica and other impurities. The crude metal was added to warm dilute nitric acid (sp. gr. 1.25), and the resulting solution evaporated to dryness in order to insure complete removal of silica. The mixture of basic nitrate and oxide was ignited till free from nitric acid, and was then extracted a number of times with strong hydrochloric acid. The solu-

* Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology. From the *American Chemical Journal*, vol. xxiii., No. 2.

tion in hydrochloric acid was filtered through asbestos, and precipitated with acid sodium sulphite. The sulphite was added slowly until the precipitate formed was black, thus showing that most of the selenium was precipitated. After the mixed precipitates of selenium and tellurium had settled, the solution was decanted, filtered, and the precipitation continued. The tellurium which had been freed from a large share of its impurities by this second precipitation was again dissolved in nitric acid (sp. gr. 1.25), and the basic nitrate obtained from the solution by crystallisation. The nitrate was twice re-crystallised. This was best done as follows:—The salt was stirred with a large amount of nitric acid (sp. gr. 1.25), heated to about 70° C. At a higher temperature the nitrate was decomposed into a mixture of amorphous and crystalline oxide, which was not readily dissolved by the acid. The solution was filtered through asbestos, and evaporated at a temperature of about 80°. In some cases the solution was allowed to cool after crystals appeared. In other cases the evaporation was continued while the crystals were separating from the liquid. By the latter method larger crystals were obtained, which were at times 0.5 c.m. in length. The nitrate crystallises in orthorhombic prisms, terminated by macrodomes and truncated by well-developed macropinacoids and small brachypinacoids. The salt is not hygroscopic, some crystals having stood in the open air for over a month without losing their bright lustre.

Purity of the Basic Nitrate of Tellurium.

The purity of the basic nitrate of tellurium, which had been twice re-crystallised, was studied. It was again re-crystallised from nitric acid, and a qualitative analysis of the crystals was made. The mother-liquor was evaporated to dryness, and also analysed. The presence of no foreign element was detected in either case. Whitehead (*Fourn. Amer. Chem. Soc.*, xvii., 849), and Keller (*Fourn. Amer. Chem. Soc.*, xix., 778), have determined what substances are present in the crude copper from which the tellurium used in this work was obtained. These are silver, gold, bismuth, arsenic, antimony, and selenium. As none of these elements forms a crystalline compound which is difficultly soluble in nitric acid, it is seen that the basic nitrate of tellurium was readily obtained in pure condition. Brauner has shown that pure tellurium cannot be obtained by precipitation, and that repeated distillation of the metal is necessary to free it from the heavy metals.

In order to test for minute traces of selenium, a common impurity in tellurium, the following method was devised, based on the difference in behaviour of the oxides of selenium and tellurium with hydriodic acid. The former oxide is reduced and iodine set free, while the latter is converted into the tetraiodide. The test is made in this way:—About 0.15 to 0.2 grm. of the oxide to be tested is dissolved in 2 c.c. of a 10 per cent solution of sodium hydroxide, and 3 c.c. of hydrochloric acid (sp. gr. 1.12) is added. The solution is then cooled to the room temperature, carbon bisulphide and 2 drops of a dilute solution of potassium iodide (2 grms. in 100 c.c. water) are added, and the tube is shaken. Under the above conditions, if selenium is present, the carbon bisulphide will be coloured by the iodine liberated, and the small amount of tellurium tetraiodide formed will remain in solution. It is necessary to avoid a large amount of potassium iodide in order to prevent the formation of much tellurium tetraiodide, which would dissolve in the carbon bisulphide, and so obscure the colour of the iodine. Any doubt whether the colour is due to liberated iodine or to tellurium tetraiodide, can be decided definitely by shaking the carbon bisulphide with water. The colour produced by the iodine is not altered while the tellurium tetraiodide is decomposed, and the carbon bisulphide again becomes colourless. The accuracy of the method was tested by mixing known amounts of selenium dioxide with the tellurium to be tested. Using the amounts given above, 0.0012 m.grm. selenium can be detected in the presence of 0.160 grm. of

tellurium dioxide, that is about 1 part in 150,000. No selenium could be detected in the oxide obtained from the pure nitrate when this very delicate test was applied.

It is of interest to note here that a strong solution of potassium iodide acidified with hydrochloric acid, is a very delicate test for tellurium. The dark colour produced is quite characteristic, resembling somewhat in strong solution the colour of platinum solutions containing iodides. The difference is readily shown, however, by dilution, when the colour produced by platinum persists as a pink, while the colour produced by tellurium disappears on account of the decomposition of the iodide.

No foreign substance was found in the tellurium from the nitrate by careful qualitative analysis, yet it was subjected to additional tests. Brauner and Wills found that the purest tellurium obtained by precipitation invariably left a residue when distilled in hydrogen. A sample of the oxide prepared from the nitrate was dissolved in pure hydrochloric acid, and the tellurium precipitated with sulphur dioxide, and washed until free from hydrochloric acid. The tellurium was then distilled in a stream of hydrogen, which was prepared by the action of sulphuric acid on zinc. The gas was purified by the method used by Wills (*Fourn. Chem. Soc.*, xxxv., 704), in preparing pure tellurium for a determination of its atomic weight. After the distillation a bright stain was left on the porcelain boat. The tellurium was re-distilled a number of times with the same result. The gray, shiny spot on the boat was not affected by hot sodium hydroxide, hydrochloric or nitric acid, and was not volatilised by the heat of a blast-lamp.

From the following experiments it was shown that this residue was due to the union of a small amount of tellurium with the porcelain of the boat at the high temperature required for the distillation. Some tellurium prepared from the nitrate was next distilled in a vacuum. After the first distillation a light gray substance was left in the boat. This was flocculent, dissolved completely in dilute hydrochloric acid and sodium hydroxide, and evidently was tellurium dioxide, which is always present in precipitated tellurium. The tellurium, when re-distilled in vacuum, left no residue, but when distilled in hydrogen a stain was left on the boat as before. Some pure tellurium, obtained by distillation in a vacuum, was heated on porcelain in a blast-lamp flame. A stain was left which was caused by the combination of a small amount of the tellurium with the porcelain. This does not take place when the metal is distilled in a vacuum, as the temperature of distillation is lower.

The oxide prepared from the nitrate was also completely volatile without leaving a residue. It was heated to redness on a platinum foil placed inside of a porcelain crucible. The above experiments show that a careful examination of the tellurium obtained by re-crystallisation of the basic nitrate did not show the presence of any known substance.

Analysis of Basic Tellurium Nitrate.

As the basic nitrate obtained by crystallisation from nitric acid is a stable substance, and is not hygroscopic as Klein and Morel have reported, a careful analysis of it was considered necessary. The water was determined by igniting the substance, which had been previously dried at 120°, in a current of oxygen for two hours. In the front part of the tube was placed metallic copper to reduce the oxides of nitrogen. The nitrogen was estimated by a method which was essentially that of Dumas. The tellurium dioxide was determined by heating the nitrate slowly until all of the oxides of nitrogen were given off, and then fusing quickly the oxide left. The decomposition of the nitrate was accomplished most conveniently by placing the platinum crucible inside of a larger porcelain crucible, which was heated by a Bunsen burner. After an hour's heating the oxide was in the form of a loose white powder. The results of the analyses follow:—

- I. 0.7975 grm. substance gave 23.25 c.c. N at 0° and 760 m.m. pressure.
II. 1.2222 grms. substance gave 37.20 c.c. N at 0° and 760 m.m. pressure.
I. 2.0530 grms. substance gave 0.0538 grm. H₂O.
II. 2.2981 grms. substance gave 0.0590 grm. H₂O.
I. 0.9491 grm. substance gave 0.7925 grm. TeO₂.
II. 0.9920 grm. substance gave 0.8282 grm. TeO₂.

	Calculated for		Found.	
	4TeO ₃ .N ₂ O ₅ .1½H ₂ O.	4TeO ₃ .N ₂ O ₅ .H ₂ O.	I.	II.
N ..	3.62	3.66	3.64	3.84
H ₂ O ..	3.49	2.36	2.62	2.57
TeO ₂ ..	82.54	83.52	83.49	83.36

The atomic weight of tellurium has been taken as 127.6 in calculating the above results. Klein and Morel (*Bull. Soc. Chim.*, [2], xliii., 198), using 129 as the atomic weight of tellurium, obtained these results:—

	Calculated for		Found.	
	4TeO ₃ .N ₂ O ₅ .1½H ₂ O.		I.	II.
N ..	3.59		3.70	—
H ₂ O ..	3.47		2.90	3.80
TeO ₂ ..	82.66		82.20	83.30
Te ..	65.57		66.10	66.50

Experiments described below show that there is no water of crystallisation in the compound. The formula therefore is best written Te₂O₃(OH)NO₃.

Decomposition of Basic Tellurium Nitrate by Heat.

Two samples of the nitrate were heated at gradually increasing temperatures in order to determine whether the hydrogen in the compound is present as water of crystallisation. The substance was heated for two or more hours at intervals of 10°, beginning at 110°. If at the end of that time the weight had changed, the heating was continued without changing the temperature until constant weight was obtained. The results follow:—

Number of hours heated.	Temperature.	Percentage loss.	
		I.	II.
12	110—170°	0.00	0.00
2	170—180	0.07	0.03
4	180—190	0.42	0.26
11	190—200	2.47	3.36
9	200—210	3.71	4.15
9	210—220	4.02	5.85
6	220—230	8.00	9.67
9	230—250	8.60	10.30
1	About 350	16.51	16.50

From the above results it will be seen that there is no loss of weight up to 170°, when a slight decomposition begins. At 190° oxides of nitrogen begin to be evolved. There was no distinct point at which the water was given off. The decomposition was gradual, both water and nitric acid being given off at the same time. The figures in the last line of the table give the results of heating two portions of the nitrate in covered platinum crucibles protected by porcelain crucibles. The results are practically the same as those obtained in the very accurate determinations described later, viz., 16.47. The oxide which was left was tested for nitric acid by phenol-sulphonic acid, and only a trace was found. It is therefore unnecessary to fuse the oxide in making a gravimetric estimation of tellurium, if it is heated in the manner described. The loss which accompanies fusion can be done away with, and more accurate results obtained. The experiments recorded above are not in accord with the statement of Klein and Morel that the nitrate begins to decompose at the fusing-point of lead.

Action of Nitric Acid on the Nitrate.

In re-crystallising the nitrate it was observed that at times a residue was left which dissolved with difficulty in

nitric acid. This residue, examined under the microscope, showed well-developed crystals in the form of octahedra, and, when ignited, it did not lose in weight. The nitrate was changed into a mixture of amorphous and crystalline tellurium dioxide. It was therefore important to study the conditions of formation of the oxide in order to be able to get crystals of the nitrate in perfectly pure condition.

Some nitrate was heated with not enough nitric acid (sp. gr. 1.20) to dissolve it. After the acid had boiled twenty-five minutes the residue was examined and found to contain no nitrate. From the hot solution a small amount of white amorphous powder separated. On evaporation of the nitric acid solution well-defined crystals of the nitrate were formed. These were shown by analysis to be free of oxide. The loss in weight on ignition was 16.51 per cent. Theory requires a loss of 16.48 per cent. The same results were obtained when nitric acid of specific gravity 1.25 was used. It will be seen, therefore, that, while the dilute acids decompose the nitrate, any crystals which are formed from it by concentration are pure nitrate. The reasons for the directions given above for the re-crystallisation of the nitrate are now evident. The nitrate is stirred with the acid (sp. gr. 1.25) at about 70° in order to avoid decomposition into the oxide, and saturation of the solvent. Crystals of the nitrate increase markedly in size when heated with concentrated boiling nitric acid, and a large amount crystallises from the oxide on cooling.

Electrolytic Deposition of Tellurium.

Schucht (*Fahresbericht*, 1883, 222, 1514) and Whitehead (*Journ. Am. Chem. Soc.*, xvii., 849) have shown that tellurium is deposited by the electric current from an acid or alkaline solution. Numerous attempts were made to get the conditions under which the deposit would be made in such a form that it could be weighed. It was deposited from hydrochloric and nitric acid solutions and from solutions of the alkali tellurites. As tellurium is nearest to antimony in the electrolytic scale, the conditions under which antimony is deposited were applied to tellurium. The precipitate was always in an amorphous flocculent condition. Some tellurium which had been deposited by electrolysis was converted into the nitrate and the loss in weight on ignition determined. This was done to determine whether the electrolysis had effected any decomposition of the element. As the loss in weight was 16.55 per cent, it was concluded that no decomposition had taken place.

(To be continued).

ON THE QUALITATIVE SEPARATION OF NICKEL FROM COBALT BY THE ACTION OF AMMONIUM HYDROXIDE ON THE FERRI- CYANIDES.*

By PHILIP E. BROWNING and JOHN B. HARTWELL.

SOME years ago F. W. Clarke (*American Journal of Science*, xlviii., 67) suggested a method for the separation of nickel from cobalt depending upon the solvent action of ammonium hydroxide upon the precipitated ferricyanides. The method may best be described by quoting from the original article:—"To the slightly acid solution containing the two metals, I first add an excess of ammonium chloride. This causes the cobalt precipitate, which otherwise would run through the filter, to fall in a denser state, and also of a much darker colour, often nearly black. I then add the potassium ferricyanide until the precipitation is complete, and afterwards agitate strongly

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. x., October, 1900.

TABLE I.

	CoSO ₄ ·7H ₂ O.	NiSO ₄ ·7H ₂ O.	KAl(SO ₄) ₃ saturated solution.	K ₂ FeC ₂ N ₆ .	NH ₄ OH (concentrated).	NaOH, solid, about the size of a pea.	Result.
	Grm.	Grm.	C.m.s.	Grm.	C.m.s.		
1.	—	0·0100	2	0·5	5	"	Heavy precipitate.
2.	—	0·0050	2	0·5	5	"	" "
3.	—	0·0010	2	0·5	5	"	" "
4.	—	0·0003	2	0·5	5	"	Distinct.
5.	—	0·0001	2	0·5	5	"	Plain.

TABLE II.

1.	0·10	—	2	0·5	5	"	None.
2.	0·10	0·0100	2	0·5	5	"	Heavy.
3.	0·10	0·0050	2	0·5	5	"	Distinct.
4.	0·10	0·0030	2	0·5	5	"	Very faint.
5.	0·05	—	2	0·5	5	"	None.
6.	0·05	0·0100	2	0·5	5	"	Heavy.
7.	0·05	0·0050	2	0·5	5	"	Distinct.
8.	0·05	0·0030	2	0·5	5	"	Plain.
9.	0·05	0·0010*	2	0·5	5	"	Faint.

* Equivalent to 0·0002 of the metal.

with a considerable excess of ammonia. Upon filtering, all the cobalt remains upon the filter, being recognised by the characteristic colour of the precipitate, and the nickel is readily detected in the filtrate by means of ammonium sulphide. If, upon filtering, the portion at first running through is turbid, it may be disregarded, or returned to the filter, that which filters through subsequently being almost invariably clear."

In making a study of this method we found two serious objections; first, the practical impossibility of obtaining a good filtration from the cobalt ferricyanide, even in the presence of the ammonium chloride, and, second, the large amount of sulphur thrown down when ammonium sulphide was added to the filtrate containing the nickel with the excess of ferricyanide.

Our first attempt was to secure, if possible, a complete separation of the precipitated cobalt ferricyanide and the dissolved nickel by filtration. This we were able to accomplish by the addition of a small amount of a solution of an aluminum salt to the original solution which held back the cobalt, and, as experiment showed, allowed the complete solvent action of the ammonium hydroxide upon the nickel salt. Amounts of nickel as small as 0·0001 gm. were detected, when mixed with the aluminum salt, by precipitating as ferricyanide, extracting with ammonium hydroxide, and testing in the manner to be described.

On turning our attention to a possible improvement in the method for the detection of the nickel, it was found that when the ammoniacal solution of the nickel ferricyanide was treated with strong sodium or potassium hydroxide solution, in the presence of an excess of potassium ferricyanide, a black flocky precipitate formed which gave no test for ferro- or ferricyanide, and gave every indication of being nickelic hydroxide. This reaction we found to afford us a most delicate test for nickel.

The method as modified by us may be described as follows:—Dissolve not more than 0·1 gm. of the salts of the two elements in about 5 c.m.³ of water, add a few drops of a saturated solution of alum, destroy any free mineral acid by neutralising with ammonium hydroxide, and make faintly acid with acetic acid. To this solution add about 0·5 gm. of potassium ferricyanide, and agitate to effect the solution of the ferricyanide and the complete precipitation of the nickel and cobalt salts. Then add about 5 c.m.³ of strong ammonium hydroxide, and filter. To the filtrate, which should have no reddish colour, add a piece of sodium or potassium hydroxide about the size of a pea, and boil. The appearance of a black precipitate, in case of very small amounts of nickel showing first as a dark colouration, indicates nickel.

The above tables give a record of the experimental results. With the precautions indicated, this method may be applied very satisfactorily.

THE ESTIMATION OF MOLYBDENUM IN IRON.

By E. DOHLER.

TEN grms. of steel, or 10 to 20 grms. of pig-iron, containing 1 to 3 per cent of molybdenum, are dissolved in 100 c.c. of nitric acid: this operation is carried out in a porcelain crucible, first on the water-bath, and finally on a sand-bath; the evaporation is continued to dryness, to separate the silica and to drive off the nitric acid, but the temperature must not be raised too high, or the molybdic acid will be volatilised.

The residue is taken up with about 100 c.c. of hydrochloric acid ($d=1\cdot19$): this solution is then heated on the water-bath and the hydrochloric acid evaporated off, adding water from time to time; finally, when all the oxide of iron is dissolved, and the quantity of hydrochloric acid remaining is not more than 10 c.c., more water is added, the solution is filtered, and the filtrate collected in a flask of about 1·5 litres capacity; the residue is carefully washed with warm water. This residue consists principally of silica; in the case of pig-iron it also contains graphite (and tungstic acid in cases of tungsten steel), and is perfectly free from molybdenum, as has been shown by numerous analyses; if it has been thoroughly washed, its proportion of silica and graphite will not be more than 1 per cent. Through the filtrate, the volume of which is about 1 litre, and which is kept at a temperature of about 80°, a good current of sulphuretted hydrogen is passed for about an hour.

The precipitation of molybdenum in the state of sulphide is very difficult to accomplish, but it can generally be done in one operation by following exactly the instructions given above. The precipitate, which consists principally of sulphur and sulphide of molybdenum, is allowed to stand for twelve hours in the liquid saturated with sulphuretted hydrogen, the beaker being well covered with a watch-glass; it is then filtered and washed five or six times with a cold solution of sulphydric acid, containing a little hydrochloric acid; the filtrate is then evaporated down to half its volume, and again saturated with sulphydric acid to make sure that the precipitation is complete. This is generally the case; if the liquid becomes dark-coloured by reason of the formation of sulphide of manganese—it should be remembered that a

trace of this sulphide suffices, like sulphide of lead, to colour the liquid—it must be left to stand for about ten hours, and then treated as above.

The precipitate is then removed from the filter, and extracted with warm sulphide of ammonium, then with warm water. If any precipitate is left, we try whether it is soluble in hydrochloric acid; if so it is sulphide of iron, and may be neglected; if it become brown, that would indicate that it contained sulphide of molybdenum, and that the extraction with sulphide of ammonium was not complete. The filter must be calcined at a moderate heat in a porcelain crucible, with a little double carbonate of soda and potash and sulphur, in the proportion of 2 to 1, and the melted mass taken up with water. Sulphide of ammonium is added to the solution, and the whole heated for two or three hours to dissolve all the molybdenum. The solution is filtered, and the residue on the filter carefully washed; the residue is treated as before. The solution of sulphide of ammonium, which should be quite clear and of a deep yellow colour, on account of the excess of sulphide of ammonium, is brought to boiling-point, and the molybdenum precipitate d by the addition of hydrochloric acid ($d=1.124$) in excess. The reaction is violent, especially if the solution is warm, on account of the evolution of sulphydric acid; therefore the hydrochloric acid should be added slowly and cautiously. The solution must then be heated until sulphuretted hydrogen is no longer given off, filtered on a filter dried at 120° , and washed until the filtrate no longer gives any reaction with nitrate of silver. The precipitate is then dried at 120° until its weight is constant.

After this weighing the precipitate is pulverised in an agate mortar. A part of the powder obtained is gently heated to redness in a current of hydrogen until its weight is constant; the pure sulphide obtained (MoS_2 , containing 60.00 per cent Mo) is then weighed.

Although this method is rather complicated, it has the advantage of giving excellent results, which is not the case, as the author has proved, with those methods given in most text-books, and which are, further, almost impracticable.—*Chemiker Zeitung*, 1900, p. 537.

NOTE ON A METHOD OF DETECTING FREE PHOSPHORUS.

By P. MUKERJI, B.Sc., Professor of Chemistry, Presidency College, Calcutta.

THE following statement is made in Roscoe's "Treatise on Chemistry" and in Watts' "Dictionary of Chemistry":—"Phosphorus does not directly combine with hydrogen."

The principle employed for the detection of free phosphorus in the present note is the phosphorescence of the vapour of phosphorus diluted with hydrogen gas.

The following is the apparatus employed:—A three-necked Woulfe's bottle; to the middle neck of which there is attached by a cork a tube about 11 inches long and of half an inch diameter, the upper end of the tube being closed with a cork. To another neck a safety funnel with a long tube is attached, and in the third neck a short jet is inserted. The tube of the safety-funnel dips into the liquid in the bottle; the middle tube and the jet enter the bottle only for a short distance. The tube attached to the middle neck is somewhat loosely fitted, so that traces of air may enter the bottle. The jet and the funnel are fitted tightly. The capacity of the bottle may be a litre or less.

For the above-mentioned apparatus a simpler one has been substituted in several experiments; namely, a small flask of about 184 c.c. capacity, and fitted with a funnel with a stopcock and also with a jet.

The Method of carrying out the Test, and the Appearance.—Zinc and dilute sulphuric acid are introduced into the bottle, and the gas issuing from the jet is observed. If in

a dark room, there is no glow perceived, then the materials employed are free from uncombined phosphorus. When the bottle is so hot, through the chemical action between the zinc and acid, that it can scarcely be touched, i.e., when the temperature of the liquid is about 60° to 70° C., and that of the gas in the upper part of the bottle is 45° to 50° C., the cork is removed from the top of the tube attached to the middle neck, and the substance suspected to be phosphorus, or to contain this in a free state, is introduced through the tube into the bottle, and then the cork is quickly inserted. If an organic mixture suspected to contain free phosphorus has to be introduced, it may be poured in through the thistle funnel, or, better still, through the neck to which the jet is attached; the jet is quickly put back into the neck after introduction of the mixture. Soon after the introduction of phosphorus (free) the gas issuing from the jet is found to glow in a dark room, a sheaf of light emanating from the jet. The liquid inside the bottle glows, and luminous flashes are also seen now and then. If now the cork at the top of the middle tube be removed, the light will sink down through the jet, and the gas escaping at the top of the middle tube will glow. On replacing the cork the glow will reappear at the jet. By alternately removing and replacing this cork, the glow may be made to move downwards and upwards through the jet at the option of the operator. (If the second form of apparatus is used, it is only necessary to take off and replace the stopcock below the funnel, and the glow will appear alternately in the funnel and at the jet).

Fresh quantities of dilute sulphuric acid and platinum chloride may be introduced if the glow shows signs of ceasing.

Delicacy of the Test.—In one experiment, 7 m.grms. of phosphorus were cut into two larger and two smaller pieces; and one of the smaller pieces (about 1.5 m.grms.) was introduced into the second form of apparatus; the appearance noted above was observed. After about half-an-hour the zinc was washed two or three times, and kept in the flask under water. About twenty-four hours later this zinc, without any further addition of phosphorus, again showed the glow at the jet and in the funnel.

In another experiment the first form of apparatus was employed, the capacity of the bottle being a little over a litre. 112 grms. of zinc, 250 c.c. of acid and water, and 30 c.c. of milk, were introduced into the bottle; next, 2 m.grms. of phosphorus were introduced. The jet, the middle tube, and the bottle, all glowed in the way described above. It may be here stated that Fresenius's limit for Mitscherlich's test is 1.5 m.grms. of phosphorus in 150 grms. of mixture; the second experiment shows that the present method is, at least, as delicate as Mitscherlich's.

Remarks on the Process.—The use of nascent hydrogen as a reagent for the detection of phosphorus is now new. Valentin mentions it in his "Qualitative Analysis," but his method is not the same as the present method. He observes the green core of the hydrogen jet after ignition, and he does not use a dark room. Moreover, his apparatus is Marsh's apparatus. His test is not a test of free phosphorus only, but indicates indifferently either phosphorus, phosphide, phosphite, or hypophosphite, since any one of these substances will give a flame with a green core on treatment with nascent hydrogen, i.e., with zinc and dilute sulphuric acid. It need hardly be stated that the method described in this paper is not the Blondlot-Dussard method, since the hydrogen jet is not ignited, and the appearance observed is not the green core of the flame of burning hydrogen. The phenomena observed in the present method are very similar to those described by Crookes in page 489 of his "Select Methods," third edition. Crookes, however, uses a somewhat complicated distilling and condensing apparatus, and employs a lamp for distilling the phosphorus; the lamp again necessitates the use of materials for preventing its light from hindering the observation of the glow. Moreover, in his method,

the glow is *not under control*. The apparatus described above is simple; no lamp is required for heating, and consequently no precaution is necessary as to the reflected light of the lamp being mistaken for the glow of phosphorus. Again, the operator can, by using the present method, make the glow move up and down as often as he likes, and with great ease. Finally, there is no risk of explosion, since hydrogen *continues* to be evolved even when air is sucked in through the jet (by opening the top of the middle tube); air cannot rush in to any large extent. Lastly, phosphorus can not only be detected by this method, but it can also be estimated quantitatively by passing the vapour thus evolved into silver nitrate solution.

After determining the exact method in which the present test is to be carried out, the influence of a good many substances upon the glow described above was tried, and by comparing the results obtained with those stated in connection with Mitscherlich's method by Crookes and others, it appears that the *present method is superior to Mitscherlich's*. This will be seen from what will be stated presently. It may be first of all noted that common bazaar zinc was used; the zinc contained some phosphorus in the combined state (and also some arsenic). Hence in contact with dilute sulphuric acid the zinc evolved a jet of hydrogen, which burnt with a green core on ignition, but which gave no glow without introduction of free phosphorus. It follows that for the *detection* of phosphorus it is not necessary to use pure zinc. It may be suggested that steam could be substituted for nascent hydrogen in the second form of apparatus described above. The objection to steam is that the glow is not as controllable as it is with nascent hydrogen; moreover, there is the risk of explosion after suction of air through the jet by removing the lamp from below the flask and *then re-heating*. The risk of explosion will be distinctly greater in presence of mustard oil, phosphoretted hydrogen, &c., and in presence of iodine, sulphuretted hydrogen, ether, &c.; nascent hydrogen has also a decisive superiority, as will appear later on. Then again, on *boiling* phosphorus in a complex aqueous mixture (when the temperature must be higher than 100° C.) some portion of the element may get oxidised by water, if by nothing else, and cannot then be vaporised.

As already stated some of the substances in presence of which phosphorus was detected by this method were such as are known to interfere with the glow in the older methods. Milk, boiled rice, flour, silica, though not included in this category, were thus tried; the glow was well observed both at the jet and at the top of the middle tube after addition of phosphorus. Sodium or potassium hypophosphite solution freshly prepared and filtered from particles of phosphorus gave no glow, though phosphoretted hydrogen was apparently evolved as the gas at the jet burnt with a green core upon ignition; the glow appeared soon after introduction of a minute piece of phosphorus. Phosphoretted hydrogen therefore does not interfere with the glow in this method. Sodium phosphite also gave no glow, though it evolved phosphoretted hydrogen. Nitrous fumes are said to stop the glow of phosphorus, but it was found that in this method nitrate or nitrate mixed with chloride did not prevent the glow. Mustard oil was tried; it did not interfere with the glow; the jet became blocked by a whitish oily deposit after some time, but there was the usual glow in the funnel (of the second form of apparatus). The gas did not take fire, and there was no explosion. Sulphuretted hydrogen and also iodine are stated to interfere with or stop the glow of phosphorus. In the present method the result obtained in presence of either of these substances may be regarded as satisfactory. In one experiment 10 c.c. of a saturated solution of iodine in potassium iodide were introduced in three portions; the glow was seen as usual, and the issuing gas did not colour starch paper to any appreciable degree. In another experiment about 4½ grms. of powdered ferrous sulphide were introduced in two portions, and about 3 m.grms. of phosphorus were used.

The glow was observed at the jet and in the funnel; next the jet was changed, and the new jet also gave the glow. Ether, alcohol, and oil of turpentine were also tried. Oil of turpentine stopped the glow altogether, but it was found that so far as the present method is concerned the failure may be easily remedied. A piece of phosphorus about 2 m.grms. was introduced into boiled rice; oil of turpentine, 2½ c.c., was next added, and then a little water, and the mixture shaken. Now the turpentine was removed by decantation after adding some water; the mixture was next quickly washed (by decantation) with alcohol, and finally with water. The mixture probably still contained traces of turpentine oil, but on introduction into the hydrogen-evolving bottle the glow was seen as usual. Next 5 c.c. of alcohol were introduced into the bottle, the glow continued at the jet, and was also observed at the middle tube, though it was a little less bright. As regards either it is as prejudicial to the glow as oil of turpentine; but there is this difference that the glow appears *after a time* on introduction of a fresh piece of phosphorus.

It may be stated here that after the experiment is over the bottle or flask used for the experiment should be filled with water before opening it in air.

It will be seen from what has been stated above that the present method will greatly facilitate the detection of phosphorus in food and in cases of poisoning. The apparatus described is simple, and zinc and sulphuric acid can be procured in any town. The glow is seen on a magnified scale, and there is no possibility of its being mistaken, especially as no lamp is required. Moreover, many substances that hinder the glow of phosphorus in the older methods do not affect the glow as observed by the present method.

I have, lastly, to state that my assistant, Haridas Saha, M.A., has helped me considerably in carrying out these experiments.—*Journal of the Asiatic Society of Bengal*, lxi., Part 2, 1900.

Estimation of the Total Sulphur in Coal.—V. Antony and A. Lucchesi.—The authors have modified Eschka's method, and proceed by heating 1 grm. of the material, 4 grms. of pure MnO_2 , 1 grm. of MnO_4 , and 2 grms. of dry NaCO_3 , in a small platinum crucible. The heat is applied gently at first, and finally increased up to a bright red. The mass is then plunged into 40 to 50 c.c. of water, acidulated with nitric acid, boiled, filtered, and the sulphate finally precipitated with BaCl_2 . The authors give a series of comparative analyses made by their method and by that of Eschka, which shows theirs to be as exact as the latter.—*Gazz. Chim. Ital.*, (1), xxix., p. 181.

The Volumetric Estimation of Sulphuric Acid.—F. Litterscheid and K. Feist.—The authors estimate sulphuric acid by treating sulphates dissolved in water with a solution of BaCl_2 (30.5 grms. of $\text{BaCl}_2 + 2\text{H}_2\text{O}$ 100 cc., the normal solution being too concentrated). The excess of chloride is precipitated by carbonate of ammonia. The liquid is then titrated with 1-roth normal hydrochloric acid.—*Arch. d. Pharm.*, ccxxxvii., p. 521.

Asbestos Filters.—O. Lohse.—The author has discontinued the use of glass-wool for filters; he proposes, instead, to use test-tubes fitted with ground stoppers, of which the bottoms are pierced with a number of small holes, and with a slight shoulder formed a few centimetres above them. The bottom of these tubes is covered with a layer of short fibres of asbestos, about 10 to 12 m.m. in thickness, which can be introduced by means of a long pair of tweezers. For suction filtering, the tube is passed through a cork fitting in another tube connected with the conical vessel in which the vacuum is made. The author has also constructed a special kind of desiccator; both these pieces of apparatus are illustrated in the original paper.—*Berichte*, xxxii., p. 2142.

NOTICES OF BOOKS.

Water in its Application to Manufactures. ("L'Eau dans l'Industrie"). By H. DE LA COUZ. Paris: Vve. Ch. Dunod. 1900. Pp. 496.

WATER plays a most important part in many manufacturing processes, and its quality, in a large number of cases, makes all the difference between success and failure. The influence of salts soluble in water ought to be more thoroughly studied by the manufacturer, so that he may be able not only to recognise the evil, but also be able to quickly apply the best means for its elimination.

It was with this end in view that the author undertook the preparation of the present volume, and the ground he covers leaves but little undone.

For the generation of steam, which is one of the widest uses to which water is put, numerous objections can be pointed out to the use of different waters; incrustations and corrosions occur which add greatly to the expense of fuel, seriously affect the steaming power of the boiler, and are a fruitful source of explosions. All these inconveniences can be prevented by a previous examination of the available water supply and the timely application of a suitable remedy.

Besides very full instructions for the analysis of water, a large portion of this work is applied to the influence, based on numerous experiments, of waters of various qualities on widely different manufacturing processes, such as dyeing and calico-printing, bleaching, wool-washing, soap-making, tanning, paper-making, photography, brewing and distilling, sugar refining, &c.

In these various industries, the waste water may often be of such a character as to make the recovery of certain portions of their contents a remunerative operation: this unfortunately is often neglected, and, besides the actual pecuniary loss to the manufacturer, the public at large also suffer from the injury done to health by the needless pollution of water supplies. In fact, such purification of waste waters is often, to his own benefit, forced on the manufacturer by public and sanitary authorities.

This work, dealing in so thorough and efficient manner with the subject, reflects the highest credit on the author for the painstaking manner in which he has brought together the large amount of information bearing on such widely differing branches of the subject.

The book is well printed on good paper, and contains numerous illustrations; it has a comprehensive table of contents, but, as is so often the case with books published in France, there is no Index.

The Air of Rooms, an Examination of the Effect produced on the Air of Rooms by the Use of Gas, Coal, Electric Light, &c., for Heating and Lighting Purposes. By FRANCIS JONES, F.R.S.E., F.C.S. Manchester: Taylor, Garnett, Evans, and Co., Ltd. 1900. Pp. 59.

THE chemists of one hundred years ago were agreed that air consisted of two gases, now called oxygen and nitrogen, and that its composition was remarkably uniform. Cavendish found only slight differences between the air of London and the air of Kensington, sometimes in favour of one and sometimes of the other, "but," he says, "the difference was never more than might proceed from the error of experiment, and by taking a mean of all there did not appear to be any difference between them." These views no longer hold good; we know now that air also contains carbon dioxide, water vapour, ammonia, and other gases, in proportions which, though variable, can nevertheless be accurately determined; in most cases, however, the determination of the quantity of carbon dioxide forms a sufficient indication of the quality of the air. The presence of this gas is due either to the breathing of animals or the burning of coal, wood, gas, or other carbonaceous material, both of which processes remove oxygen from the air and form carbon dioxide.

The estimation of carbon dioxide in air is not at all a difficult matter, and is now generally done by what is known as Pettenkofer's process, and it is also now generally agreed that good air, away from towns, contains about 3 volumes of carbon dioxide per 10,000 of air.

The problem of the air of rooms is, however, a very different one to that of the outer air. Indoors the products of respiration and combustion are not removed rapidly, even by the best systems of ventilation, and in many cases they accumulate to such an extent as to become injurious to health.

For the purpose of thoroughly investigating this matter the author fitted up a small room, which was devoted entirely to this investigation. The air space was 935 cubic feet; it had one fireplace, one window, and a ventilator at the roof opposite the door. This ventilator, 18 inches by 9 inches, was always kept open.

Determinations were made of the amount of carbon dioxide at different times of the day, and also of the amount of moisture in the air.

Eleven sets of experiments were made, numbered A to K, under varying conditions, such as—Set A. Coal-fire in use; room lighted with gas. Set D. Gas-fire in use; room lighted with the electric light. Set H. Gas cooking-stove in use (oven), draughting into chimney. Two Bunsen lamps in use; &c. The tests were made of the air at the level of the table, as it is as a rule, says the author, nearest the position where the air of a room is inhaled. We think the author is mistaken here, as the breathing level in a room is decidedly higher than the table level. Full details of these and other experiments are given, and the results are set out in tables and curves at the end of the pamphlet. The author arrives at a number of conclusions as the result of his investigations, among which may be mentioned "The air of a room, however lighted and heated, is purest at the floor, less pure 3 feet above, and most impure at the ceiling." This is exactly what we should have expected, and in fact may be looked upon almost as a matter of common knowledge. He also finds that a coal fire and the electric light is the best method of heating and lighting a room; gas fires diminish the humidity, and the use of gas cooking-stoves—even when draughting into the chimney—greatly increases the amount of carbon dioxide in the air of a room.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 14, October 1, 1900.

Absorption of Free Oxygen by Normal Urine.—M. Berthelot.—The author examined various urines, and found that they all absorb free oxygen to a greater extent than pure water. Under the conditions of his experiments, as much as 22 c.c. per litre was found to be absorbed. Urine behaves as a reducing liquid. In this respect it is like the greater number of the tissues of the body, with this difference that the other tissues exist before the arterial blood passes through them and take up a portion of the oxygen from this blood, whilst urine, on the contrary, is extracted from the blood itself. The absorption of oxygen observed in this set of experiments is a true chemical phenomenon, and it is not due to the agency of microbes, such as that producing acetic fermentation.

Acidity of Urine.—M. Berthelot.—The acidity of urine is usually measured by means of phthalein, and compared with a certain equivalent weight of sulphuric acid. This method, however, needs some modification. To be accurate this weight ought to be replaced by an equivalent

sum of those acids in urine which are susceptible of being estimated by means of phthalein; but this sum includes several orders of acidity, the acidity of the strong acids, such as hydrochloric and sulphuric, which can be accurately estimated with most common indicators, and the acidity of the feeble acids, such as carbonic acid (in the form of bicarbonates), which can be estimated accurately only with certain indicators. So when examining the spectrum it is necessary to use several indicators and compare the results.

Selenides of Nickel.—M. Fonzes-Diacon.—Selenium vapour reacts at a red heat on powdered nickel, and gives, according to Little, a crystalline mass apparently formed of crystals belonging to the cubic system. The author prepares a series of nickel selenides, analogous to the corresponding sulphides. He obtains the proto-selenide of nickel in very well defined cubic crystals; also the sesqui-, bi-, and sub-selenides of nickel. He finds that hydrochloric acid, even when concentrated and boiling, attacks all these selenides very slightly. Gaseous hydrochloric acid slowly transforms them, at a high temperature, into nickel chloride. Nitric acid oxidises them, giving the selenites. Chlorine easily displaces the selenium at a high temperature. Heated in a current of oxygen for some time, the green oxide of nickel is produced and selenious anhydride. Reduced with hydrogen at a bright red heat, all these bodies give rise to filiform nickel.

Oxycelluloses of Cotton, Flax, Hemp, and Rush Pulp.—Léo Vignon.—The celluloses extracted from cotton, flax, hemp, and rush pulp give practically the same products on oxidation. The differences, established numerically between the properties of the oxycelluloses obtained in the various cases, are relatively slight, and can be explained either by the conditions of the particular physical state of each textile, or by the condensations of the molecule $(C_6H_{10}O_5)_n$, which are not always identical for the various textiles considered. The author examined these various products with regard to oxidation, formation of osazones, reducing power, and fixation of basic colouring matters.

MEETINGS FOR THE WEEK.

THURSDAY, Nov. 1st.—Chemical, 8. "Dehydrohomocamphoric Acid and its Oxidation Products," by Arthur Lapworth. "Derivatives of Ethyl α -Methyl- β -phenylacrylate," by W. Carter and W. Trevor Lawrence. "The Nitration of Acetamino-*o*-phenylacetate (Diacetyl-*o*-aminophenol)"—a Correction, by R. Meldola, F.R.S., and Elkan Wechsler. "Rhamnazin and Rhamnetin," by A. G. Perkin and J. R. Allison. "Luteolin" (Part II.), and "Genistein" (Part II.), by A. G. Perkin and L. H. Horsfall. "Colouring-matter of the Flowers of *Delphinium consolida*," by A. G. Perkin and E. J. Wilkinson. "The Action of Alkalis on the Nitro-compounds of the Paraffin Series" (Part II.), by Wyndham R. Dunstan, F.R.S., and Ernest Goulding, B.Sc. "Hexachlorides of Benzonitrile, Benzamide, and Benzoic Acid," by F. E. Matthews. "The Influence of Solvents on the Rotation of Optically Active Compounds" (Part I.), by T. S. Patterson. "Note on Gallinck's Amidomethylnaphimidazole," by R. Meldola, F.R.S., and F. H. Streetfield.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2136.

KRYPTON II.*

By Prof. A. LADENBURG and Dr. C. KRÜGEL.

IN continuation of our recent communication on this rare element, we desire to state that we have *not* succeeded in finding any better or shorter method of preparing krypton.

If, as was described in the previous communication, 3 litres of liquid air be allowed to stand for some days in a silvered Dewar flask, and then decanted from the semi-solid paste which separates, the gas collected on allowing the residue to evaporate contains very little carbon dioxide, and, as a closer investigation showed, in addition only oxygen (about 70 per cent), nitrogen (about 28—29 per cent), and argon (about 1 per cent).

After drying, this gas was freed from oxygen and nitrogen by repeatedly leading it over red-hot magnesium previously freed from hydrogen and nitrogen, and then over heated copper oxide. In order to remove the last traces of nitrogen it was mixed, as before, with oxygen, and sparked over potash. When freed from oxygen, dried and collected over mercury, about 1 per cent of the original volume of gas remained. This was condensed by means of liquid air, and gave a clear liquid *without any trace of crystals*. This boiled from about -181.2° to -174° , and was thus almost pure argon, containing at most only traces of krypton.

A similar result was obtained on investigating the residue from the Dewar flask fitted to Linde's apparatus. Here, also, on condensation, an entirely liquid product was obtained, boiling below -170° .

From this it may be concluded that the whole of the krypton of the atmosphere is contained *in solution* in liquid air, and that the latter does not contain much more than we have isolated from it. Since we began with 850 litres of liquid air, and, according to our earlier determinations (*Ber.*, xxxii., 1415), 1 litre of liquid air weighs about 1 kilogram., the amount of material used was about 850,000 grms. From this we obtained about 32 c.c. of krypton, i.e., 0.083 grm., which amounts to only 0.0000001 or 0.00001 per cent of the material used. If it be assumed, which is not probable, that half the krypton was lost in working, the upper limit of the proportion of krypton in the atmosphere is 0.00002 per cent.

When the great scarcity of krypton had been established by this research, and there was no prospect of obtaining larger quantities of the substance, it appeared to us to be important to still further test the uniformity of our product, which had been reduced by continued sparking and in preparing a large number of spectrum-tubes to 23 c.c. For this purpose a further fractionation appeared to be the best method. The gas was therefore again condensed by means of liquid air. The condensation-tube became coated with a crystalline layer, but no liquid was produced. By decreasing the pressure and increasing the temperature, the solid was then made to evaporate, and the product was collected in two gasometers, about a third being collected in the first and the remainder in the second vessel. A density determination was then made of the gas in the second vessel.

The following data were obtained:—Weight of gas, 0.0183 grm.; volume of bulb, 7.55 c.c.; temperature, 18° C.; reduced barometer pressure, 745.4 m.m. The density relatively to oxygen = 32, or the molecular weight,

calculated from these data, is 59.01, a result which is in agreement with the numbers 58.81 and 58.67, previously found.

We are therefore justified in concluding that our gas is free from nitrogen and argon, or contains only traces of these, and our hypothesis as to the position of krypton in the periodic system is undoubtedly confirmed by this research. Probably our gas may contain xenon, but the observed density of krypton would then be too high.

THE ESTIMATION OF MANGANESE AND CHROMIUM IN TUNGSTEN ALLOYS.

By FRED. IBBOTSON and HARRY BREARLEY.

THE estimation of manganese by oxidising the nitro-sulphuric solution of the sample with lead peroxide and titrating the permanganate formed, is rapid and accurate for the materials to which it is usually applied. It could be applied to the estimation of manganese in metallic tungsten powders and such tungsten alloys as Fe-W and W-Ni, if it were not that these materials are only partially soluble in the acids usually employed.

By pouring about 10 c.c. of hydrofluoric acid over 1 grm. of the powdered tungsten or tungsten alloy in a platinum basin, adding a few c.c. HNO_3 , and when the reaction slackens 2 or 3 c.c. H_2SO_4 , it goes into solution very easily, and may then be transferred to a beaker, oxidised and titrated with FeSO_4 and KMnO_4 as usual.

The results by this process could be trustworthy only in case the hydrofluoric acid did not react with the permanganate formed; that it does not so react to the detriment of the process was proved by adding 5 and 10 c.c. HF respectively to the solution of a steel containing exactly 0.50 per cent of manganese. The results were 0.495 and 0.504 per cent Mn. And again, to the solution of 1 grm. of W powder obtained in the above manner was added varying amounts of standard manganous sulphate solution. The results calculated to percentages were—

Added.	Found.
0.09	0.08
0.19	0.19
0.38	0.36
0.47	0.46
0.56	0.54

Both tungsten powder and tungsten alloys contain generally only such manganese as is incident to the process of manufacture, and it is less than a half per cent in amount. The glass vessels are hardly attacked by the diluted hydrofluoric acid.

This process cannot be applied to those self hard alloys which occasionally contain as much as 10 per cent of manganese, except by working on less than a decigram. of the material. The chlorate process can, however, be applied if the HF be first boiled off; but it is necessary to remember that the chlorate process, as commonly carried out, gives low results with high manganese alloys, on account of the precipitate containing less oxygen than corresponds to MnO_2 . Both Norris (*CHEM. NEWS*, lxiv., 242) and Ford and Bregowky (*Journal Chem. Soc.*, lxxiv., ii., 540) have used hydrofluoric acid to assist the decomposition of silicious bodies: the latter maintain that the presence of HF assists the precipitation of the manganese.

The Estimation of Chromium.

The alloys of iron, chromium, tungsten, and manganese, which are melted up with iron to produce self-hard steels, are not decomposed by sulphuric or nitric acid, or a mixture of the two, as alloys usually are to which the acid permanganate oxidation, commonly known as Galbraith's process, or Stead's modification of it, are applied,

* Communicated by Prof. van 't Hoff to the Akademie der Wissenschaften zu Berlin, July 5, 1900. Compare *CHEMICAL NEWS*, May 4, 1900, p. 205.

Such alloys may be easily decomposed by acid mixtures containing hydrofluoric, but it is desirable—though not necessary in some cases—to get rid of the hydrofluoric acid again before proceeding to the permanganate oxidation.

Generally the presence of hydrofluoric acid is objectionable, because—unless a large amount of manganous salt is in solution—small additions of permanganate are not decolourised by vigorous boiling when only a small fraction of the chromic oxide has been converted to chromic acid; and, if by the presence of much MnO in solution the permanganate does become all decomposed, the supernatant solution has a clear yellow colour only when a large MnO_2 precipitate has been formed. If a small precipitate only is formed, the filtered solution has a brown colour, due to dissolved MnO_2 or some oxide of manganese higher than MnO . Since the addition of so much permanganate as forms large precipitates carries down some of the chromic acid, Galbraith's process is not trustworthy under these circumstances. But Stead's modification of it, in which the precipitated MnO_2 , purposely a large one, is dissolved in dilute hydrochloric acid and the chlorine boiled off, gives quite satisfactory results when no nitric acid is present in solution.

In order to avoid the use of nitric acid, the sample, after digesting with a mixture of sulphuric and hydrofluoric acids, is treated with a few grms. of permanganate crystals: in moderately dilute solutions the reaction is very rapid, but it is essential, unless capacious platinum basins are available, to transfer to a flask, dilute, and boil with an excess of permanganate until all the metal is gone.

Another method, which is just as expeditious, is to decompose the sample with fluor-nitric acid, add sulphuric, and boil down over a Bunsen until SO_2 is evolved. The sample may then be diluted and completed by either process. A further advantage of this mode of opening up the sample is, that after dissolving up the precipitated MnO_2 with HCl , the tungsten may be estimated by filtering off the WO_3 : the chlorine is boiled from the filtrate all the more quickly for its absence.

The Technical Department,
University College, Sheffield.

THE REDUCING ACTION OF DENITRIFYING BACTERIA.

By G. AMPOLA and C. ULPANI.

THIS research has been carried out principally on the bacteria which give off nitrogen with the nitrates, especially the *Bacillus denitrificans* V., or *pseudo-pyocyanic*.

Nitrogen combined with hydrogen in the form of ammonia or amine is not set free by the ferment.

Hydroxylamine and hydrazine interfere with the development of the bacteria.

The organic nitrates which are non-saponifiable in aqueous solution, such as nitromethane, remain unattacked.

The saponifiable organic nitrates, such as nitrate of ethyl, are gradually attacked during the saponification.

Among the ionisable nitrates, nitric acid with the ion H is not attacked, even in centinormal solution. The following nitrates are decomposed in the following order, commencing with the one that is the most easily decomposed:—Nitrates of caesium, rubidium, potassium, sodium, lithium, barium, strontium, calcium, magnesium, and glucinum.

The other metallic nitrates are not attacked.

The nitrates of the organic bases, strychnine, cocaine, &c., are rapidly reduced.

The authors propose classifying the denitrifying bacilli in three categories:—

1. Those which destroy nitrates alone.
2. Those which only attack nitrites.
3. Those which act on both nitrates and nitrites.

They have also examined the action of the denitrifying bacilli on arseniates which are reduced to arsenites, on chlorates which give traces of chlorides, and on ferricyanides which are easily reduced to ferro-salts.—*Gazz. Chim. Ital.* [1], vol. xxix., p. 49—72.

NOTE ON M. FITTICA'S TRANSMUTATIONS.

By C. R. GYZANDER,
Chemist to the Cochrane Chemical Co., Boston, U.S.A.

THOUGH I presumed that M. Fittica was sincere when I read his first article about "Transmutation of Phosphorus into Arsenic" (*CHEMICAL NEWS*, vol. lxxxi., p. 257), I nevertheless had the impression that there was a mistake somewhere. When M. Winkler, a little later, showed where the error lay, I was looking forward to Mr. Fittica's acknowledgment of his mistake.

The *CHEMICAL NEWS* of October 5th gave the expected reply from M. Fittica, but, instead of admitting an error on his part, he seems to think that the error is really M. Winkler's. He not only clings to his former statement, but adds that he has succeeded in bringing about another transmutation, that of phosphorus into antimony. M. Fittica, in his first paper, starts from the assumption that his red phosphorus was free from arsenic, "as tested above."

M. Winkler has shown, very conclusively, that those methods, included in "as tested above," are of no value unless properly carried out. Nevertheless M. Fittica, in his second article, says, "Has M. Winkler proved that my methods are inexact or false? In no way." He certainly has in the eyes of most chemists. What is really needed is for M. Fittica to give better proofs that his phosphorus and other reagents are free from arsenic. Though M. Fittica lays great stress on implicitly following his directions, it would have been of inestimable value to him if he had carried out M. Winkler's suggestions in establishing the absence of arsenic.

To publicly state one's belief in, or acceptance of, any hypothesis may be all very proper. To work and search a life-time for facts, by which to prove its correctness, is heroic. One expects learned men to busy themselves with even apparently impossible things, and, to those who do, disappointment and failure should not be surprises. But, on the other hand, one also expects that a man of science should be able to distinguish truth from mere appearance, or, if not, that he should acknowledge the error when it is pointed out to him.

Though I am not in a position to contest the possibility of transmutations generally, or of the doctrine that our elements are compounds, formed by atomic or molecular combinations of one or more truly elementary bodies,—theories which may possess great charm, yet I do know that we are not in possession of any experimental data, including M. Fittica's statements, which might lead us to assume that transmutations are to be transferred to the domain of actual facts.

The reaction which, according to M. Fittica, appears to take place in transmuting phosphorus into arsenic is— $2P + 5NH_4NO_3 = (PN_2O)_2O_3 + 10H_2O + 3N_2$. How does he know that? Why it could not equally well have been $2P + 5NH_4NO_3 = (PN_2O)_2N_3 + 10H_2O + 3NO$, for example, will never be clear to me, unless the latter, or something similar, is reserved for the antimony transmutation. Assuming that it was possible to prepare M. Fittica's hypothetical PN_2O , and that it gave some reactions resembling those of arsenic, it would nevertheless be vastly different from a transmutation. But M. Fittica has not given the slightest evidence to show that the compound obtained by him, and which gave reactions

similar to arsenic, had the composition PN_2O , save the above hypothetical reaction. If the cosmic changes which produced our elements were of such simple nature as indicated in M. Fittica's transmutations, one might assume that the reverse reaction, $\text{As} = \text{Px} + \text{Ny} + \text{Oz}$, was equally readily induced.

If, therefore, M. Fittica can show that arsenic is composed of phosphorus, nitrogen, and oxygen, he will have the means of proving that his assumed reaction is possibly correct, and that a transmutation takes place. Unless M. Fittica can produce better evidence than has been so far submitted, I for one must believe that his conclusions are based on misplaced confidence.

At present the subject may be summed up in the following words:—Unless we do exactly as M. Fittica did, and reason as he did, we shall probably never be able to realise the truth of transmutations. M. Fittica informs us, in his reply to M. Winkler, that he shall have more to say, later on, concerning the antimony transmutation. Assuming that M. Fittica is equally convinced of the possibilities in this direction, I would venture to suggest that, as the yield of transmuted antimony was so slight, from the phosphorus employed, it might prove advantageous to search amongst the safety matches for reagents to assist in bringing up the yield.

THE RELATIVE VALUES OF THE MITSCHERLICH AND HYDROFLUORIC ACID METHODS FOR THE DETERMINATION OF FERROUS IRON.*

By W. F. HILLEBRAND and H. N. STOKES.

AMONG determinations in mineral and rock analysis, upon the accuracy of which great stress is laid, is that of iron in the ferrous condition. It is of special importance, because an error attaching to it affects in like degree, but opposite direction, the ferric iron that is also nearly always present. Up to about the year 1867, the only method for its determination giving at all satisfactory results was that of A. Mitscherlich (*Journ. Prakt. Chem.*, 1860, lxxxi., 116), depending on the decomposition of the mineral at high temperature by rather strong sulphuric acid (3 parts acid to 1 part water by weight) in a sealed tube from which air has been expelled, and subsequent titration of the ferrous iron by permanganate. When pure hydrofluoric acid became a commercial article, the above method gave place in large measure to one depending on the decomposition of the silicate by a mixture of dilute sulphuric and hydrofluoric acids at atmospheric pressure and a temperature not above 100° C., care being taken as before to prevent contact with air (*J. P. Cooke, Am. J. Sci.*, 1867, [2], xliv., 347).

It became known in the laboratory of the United States Geological Survey, fully twelve years ago, that the two methods generally give discordant results when applied to the same rocks, the Mitscherlich method in such cases always showing the higher figure for ferrous iron. With low percentages of iron the discrepancies were not very great, but they seemed, in general, to increase as the ferrous oxide rose, until, with a rock showing 10 per cent ferrous oxide by the hydrofluoric acid method, the Mitscherlich method might give 12 per cent. Experiments with artificial ferrous salts threw no light on the subject, for both methods gave with them the same sharp and concordant results.

Until very recently no cause suggested itself whereby the discordance could be explained. In theory, the Mitscherlich method seemed perfect, and it was concluded that, given entire decomposition of all ferruginous minerals,

the determinations made by it were nearer the truth than those by the hydrofluoric acid method. That the reverse is true, in most cases, appears as the result of work done in this laboratory in an entirely different connection.

In the first place it had been found, by long experience, that nearly all rocks carry small amounts of sulphides—pyrite, pyrrhotite, or both—often visible to the eye, but more often in such small amount as to escape direct observation. One of us (Stokes), in an investigation now in progress on the oxidising action of ferric salts on sulphur, pyrite, and other sulphides, has found that this action is vastly more rapid and complete than has hitherto been suspected; that not only is the metal of the sulphide oxidised, but the sulphur to sulphuric acid as well.

The application of these observations to rock analysis shows that the presence of 0.01 per cent of sulphur in any unoxidised form may produce a maximum error of 0.135 per cent in the ferrous oxide determination, and the not infrequent amount of 0.10 per cent of sulphur will multiply this error by 10. One atom of sulphur (32) requires for its complete conversion into trioxide the oxygen of 3 molecules of ferric oxide (480), which then becomes 6 molecules of ferrous oxide (432). The case is still worse with the sulphide, since not only the sulphur, but its accompanying metal must be oxidised. The above percentages of sulphur evolved as hydrogen sulphide, and fully oxidised, would involve errors in the ferrous oxide determination of 0.18 per cent and 1.80 per cent respectively. The error caused by sulphides tends to become greater the more there is present of either or both sulphide or ferric salt. Now the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively rich in pyrite and pyrrhotite; hence the increased discrepancy between the results by the two methods, as the iron contents of the rock rise, is fully in accord with the above explanation.

The following experiments made by Stokes (somewhat out of their contemplated order in his investigation referred to) bear out the above statements most fully, and show that the Mitscherlich method for rocks and all minerals which contain even a trace of free sulphur or sulphides is no longer worthy of a moment's consideration.

Experiment 1.—0.0010 gm. pyrite was heated with 25 c.c. of a sulphuric solution (1 part acid to 3 parts water by weight) of ferric ammonium sulphate (0.0470 gm. of ferric oxide) in a horizontally-lying sealed tube for six hours at 175° to 195° C. All air had been carefully replaced by carbon dioxide. The pyrite had nearly disappeared, and titration with permanganate showed a consumption of oxygen equivalent to 0.0058 gm. ferrous oxide. Complete oxidation of the pyrite would have required oxygen equivalent to 0.0090 gm. ferrous oxide.

Experiment 2.—This was exactly like the first, except that 0.0013 gm. pyrite was used. Permanganate was reduced equivalent to 0.0090 gm. ferrous oxide. Had oxidation been complete the figure would have been 0.0117 gm.

It is quite possible that in both of these experiments the oxidation would have been complete had the pyrite been disseminated throughout a greater space in the tube, as is the case when rocks and minerals are treated, because of the presence of a gm. or thereabouts of diluting quartz and silicates.

Had precisely similar experiments been made with rock powders carrying 0.10 per cent, and 0.13 per cent, of pyrite with 4.7 per cent of ferric oxide and no ferrous oxide, the following erroneous results might have appeared:—

	I.	II.
Ferrous oxide	0.68	0.91
Ferric oxide	4.00	3.76

To overcome the possible objection that the foregoing experiments were not conclusive as to the worthlessness of the Mitscherlich method in presence of sulphides be-

* Published by permission of the Director of the United States Geological Survey. From the *Journal of the American Chemical Society*, vol. xxii., No. 10.

cause the concentration of the acid was very different from the normal, the following sealed tube experiments were made with acid of the normal strength (3 parts acid to 1 part water by weight) without any ferric salt, the belief being that the stronger acid, under the conditions of the experiment, would itself act as an oxidiser.

Experiment 3.—Pyrite 0.0016 gm. Three hours at 195° C. Solution only partial. Consumption of permanganate equivalent to 0.0017 gm. ferrous oxide.

Experiment 4.—Pyrite 0.0032 gm. Twelve hours at 220° C. Solution perfect. Odour of sulphur dioxide apparent on opening tube. Consumption of permanganate equivalent to 0.01742 gm. ferrous oxide.

Experiment 5.—Sulphur 0.0021 gm. Three hours at 195° C., and, as the sulphur had not disappeared, further six hours at 250° C. Entire disappearance of the sulphur. Consumption of permanganate equivalent to 0.01320 gm. ferrous oxide.

Experiment 6.—Sulphur 0.0039 gm. Twelve hours at 220° C. Entire disappearance of the sulphur, and strong odour of sulphur dioxide on the opening tube. Consumption of permanganate equivalent to 0.03619 gm. ferrous oxide.

In experiments 4, 5, and 6, where decomposition was complete, the consumption of permanganate is considerably less than theory requires, but this is explained by the escape of not a little sulphur dioxide on opening the tube. Had a ferric salt been present the consumption of permanganate would undoubtedly have reached that required by theory.

It might be supposed, from the foregoing, that a similar error would affect ferrous iron determinations by the hydrofluoric acid method. However, experiment has shown that with the amounts of sulphide usually found in igneous rocks, their effect is negligible, though by increasing the amount of sulphide the effect becomes more and more apparent because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the Mitscherlich method, on the other hand—a temperature of 150°–200° C., and even higher, high pressure, much longer time of action, and impossibility of escape of any hydrogen sulphide that may be formed—the sulphur of the sulphides becomes nearly, if not quite, fully oxidised to sulphuric acid, at the expense of the ferric oxide in the rock, with the production of an equivalent amount of ferrous oxide in addition to that resulting from the iron of the sulphide itself.

In order to obtain quantitative data regarding the effect of pyrite on the ferrous iron estimation by the hydrofluoric acid method, the following tests were recently made by one of us.

Part of a fine crystal of pyrite was rather finely powdered and boiled out with dilute sulphuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, or from superficial oxidation of the powder, since a second boiling with fresh acid afforded a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverised. A quarter of a gm. of it, when treated with dilute sulphuric and hydrofluoric acids in a large crucible by the Cooke method for ferrous iron, then rapidly filtered through a very large perforated platinum cone fitted with filter-paper, required but two drops of a permanganate solution representing only 0.0032 gm. ferrous oxide to the cubic centimetre.

That the error obtaining under the conditions prevailing in rock analysis might be ascertained, successive portions of 1 gm. each of a hornblende schist free from sulphur and carrying 10.09 per cent ferrous oxide as the mean of several determinations and 4 per cent ferric oxide, were mixed in a 60 c.c. platinum crucible with 0.02, 0.025, and 0.10 gm., respectively, of the above purified pyrite powder. This mixture was then treated with hydrofluoric and sulphuric acids as above, the water-bath being at boiling heat for one hour. The cooled contents of the crucible were poured into a platinum dish containing water, and titrated

rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end-reaction by its reducing effect upon the permanganate, the solution was filtered as above, and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70 per cent ferrous oxide. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous iron estimation by the Cooke method is negligible. At the same time it is to be borne in mind that with increased content, either of ferric iron or of pyrite, an increased amount of pyrite will be attacked, and that the extent of this attack is undoubtedly influenced by the degree of fineness of the pyrite powder.

All users of the method have noticed the rapid disappearance in hydrofluoric solutions, when titrating ferrous iron, of the pink colour produced by an excess of permanganate. If much ferrous iron be present, many cubic centimetres of permanganate can be added without causing more than a transitory pink coloration. The solution takes on, however, in ever-increasing intensity, the red-brown colour characteristic of manganic salts. It seems that manganous fluoride in acid solution is very susceptible to oxidation by permanganate, for the above-mentioned changes take place when permanganate is added to sulphuric and hydrofluoric acids containing some manganous sulphate.

NOTES ON

LECTURE EXPERIMENTS TO ILLUSTRATE EQUILIBRIUM AND DISSOCIATION.*

By JULIUS STIEGLITZ.

I. EQUILIBRIUM AND GASEOUS DISSOCIATION.

THE prominent rôle played by conditions of ionic equilibrium in solutions of electrolytes makes a thorough presentation of the subject desirable in college courses on general chemistry, and a still more exhaustive study necessary in analytical chemistry. The relative size of the dissociation constants, and the influence exerted on the condition of equilibrium by increasing the concentration of one of the dissociation-products, are the points most emphasised. It seems desirable to impress these two points on the mind of the student at the stage where the general subject of equilibrium and dissociation is first dealt with, which may, perhaps, be done best in connection with the question of gaseous dissociation, raised, for instance, by the vapour-density determinations of phosphorus pentachloride, ammonium chloride, &c. The following two lecture experiments, with phosphorus pentabromide and phosphorus trichlorobromide,† were developed to illustrate the second of the two points mentioned, the effect of an increase of the concentration of one of the products of gaseous dissociation. The contrast of the tubes showing the dissociation of the pentabromide and the trichlorobromide at 50° may also serve to demonstrate the first point, the influence of the relative size of the dissociation constant or the relative ease of dissociation, in default of substances for which the constants for gaseous dissociation have actually been determined, and which could at the same time be used for lecture experiments in general chemistry.

Phosphorus Pentabromide and Phosphorus Tribromide.

The effect of an excess of phosphorus tribromide on the dissociation of the pentabromide is shown by comparing

* Contribution from the Kent Chemical Laboratory of the University of Chicago. From the *American Chemical Journal*, vol. xxiii., No. 5.

† Vide Wurtz's work on phosphorus pentachloride, *Ber. Deutsch. Chem. Ges.*, iii., 572.

the intensity of the colour of the bromine vapour in two tubes charged as follows* :—

Sealed bulbs containing 0.029 grm. bromine (1 molecule) and 0.058 grm. phosphorus tribromide (a little more than 1 molecule) were placed in a piece of thick-walled tubing† closed at one end, the tube drawn out to a capillary, the air exhausted to 30 m.m. pressure, and the capillary sealed rather close to the tube, the rest of the capillary being bent into a loop. The tube charged in that way was 18 c.m. long, and had a capacity of 40 c.c. By vigorous shaking the bulbs containing the bromine and tribromide were broken. A second tube of the same size was charged with 0.029 grm. bromine (1 molecule) and 0.45 grm. tribromide (9 molecules). A few coils of lead or fuse wire were wound around the lower part of the tubes.

The tubes, thus prepared, are suspended side by side in a tall beaker of water by means of the glass loops at the upper ends. A glazed white porcelain tile placed in a slightly slanting position behind the beaker makes the comparison of the colours easier. On heating at 50° only a very slight colour appears in the first tube (see below, phosphorus trichloridibromide), none in the second tube. From 80° to 90° the dissociation has progressed to the most favourable stage for comparison. The first tube shows a more intense colour than the second one, which contains the excess of the tribromide, the colour of the former being reddish-brown and opaque, while that of the latter is reddish-yellow, through which the white of the tile can still be seen.

Phosphorus Trichloridibromide and Phosphorus Trichloride.

The difference in colour between the two tubes in the above experiment will be sufficiently evident to most students, but perhaps not quite marked enough for the student whose judgment is still to be developed. By using phosphorus trichloridibromide‡ with and without an excess of the trichloride greater differences in colour were obtained, putting the student in question out of temptation to rely less on his own judgment than on the demands of theory.

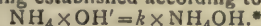
Tubes of the same size (40 c.c. capacity) were charged as above, respectively with 0.029 grm. bromine (1 molecule) and 0.029 grm. phosphorus trichloride (0.004 grm. more than 1 molecule), and with 0.029 grm. bromine (1 molecule) and 0.155 grm. phosphorus trichloride (6 molecules); the air pressure in the tubes was reduced to 27 m.m. At 40°–55° the difference in the colours of the two tubes is most marked, the first one being dark brown and the second one yellow.

The influence of the relative size of the dissociation constants, or the relative ease of dissociation of phosphorus pentabromide and of phosphorus trichloridibromide, is shown by comparing, at 50°, the colours of the tubes containing these substances (the first tube in each series); the former is found to be nearly colourless, while the latter is dark brown, showing the greater tendency of the trichloridibromide to dissociate.

II. EQUILIBRIUM AND ELECTROLYTIC DISSOCIATION. AMMONIUM HYDROXIDE AND SOLUTIONS OF AMMONIUM SALTS (AMMONIUM IONS).

Lovén (*Ztschr. Anorg. Chem.*, xi., 404) has shown that the characteristic action of ammonium salts in preventing the precipitation of magnesium hydroxide by ammonium

hydroxide is simply the result of equilibrium changes. The most important of these is the gradual suppression of the hydroxyl ions of the ammonium hydroxide by greatly increasing the concentration of the ammonium ions on adding the easily dissociating ammonium salts, equilibrium being established according to—



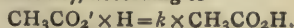
This important action of ammonium salts can be demonstrated very simply by the following experiment† with phenolphthalein. After producing a brilliant red colour by adding a drop or two of dilute ammonia to each of two beakers containing water and a little phenolphthalein, a few drops of a rather concentrated solution of ammonium chloride are added to the contents of one of the beakers. The colour fades to a scarcely perceptible pink, and then disappears.

As ammonium chloride is liable to have an acid reaction, ammonia may be added to its concentrated solution until a little of it can be shown to give a faint but distinct pink colour to a solution of phenolphthalein—proving that it certainly contains no free acid. On adding a few drops of this somewhat alkaline ammonium chloride solution to the crimson solution produced by a drop of ammonia, the red colour instantly gives way to a faint pink. This form of the experiment seems to be the most convincing and striking one; the adoption of either form must depend on the advancement of the class.

It may be added that ammonium chloride solutions which react distinctly alkaline to litmus (see below) make the red colour produced by the action of ammonia on phenolphthalein disappear completely. These experiments are, of course, based on the well-known lack of sensitiveness of phenolphthalein towards hydroxyl ions.

With analytical students the experiment just described may well be followed by a parallel experiment with litmus solution; it is best to use four beakers containing neutral litmus solution; the first is used to preserve the original tint; to the second 5 to 10 c.c. of a concentrated ammonium chloride solution are added, which, to avoid the suspicion of acidity, has been made very slightly alkaline; the colour in this second beaker changes distinctly towards a bluer violet. The other two beakers are each treated with a drop of quite dilute ammonia, which gives to each a pure blue tint, and to one of them 5–10 c.c. of the solution of ammonium chloride are added, the colour reverting to violet. The change is perfectly plain; but, as litmus is more sensitive to hydroxyl ions than phenolphthalein, the change is not as pronounced as when the latter is used.

Küster (*Ztschr. Elektrochem.*, iv., 110) has described a lecture experiment to show, by means of methyl orange, the analogous suppression of the hydrogen ions of acetic acid by adding acetate ions in the form of an acetate (e.g., sodium acetate), according to—



In consequence of hydrolysis sodium acetate reacts alkaline, and the experiment in its original form is, perhaps, open to this objection. A convincing and striking proof of its correctness may be given by using a solution of sodium acetate which, to prevent the suspicion of alkalinity, has been made very slightly acid, giving with methyl orange the well-known reddish-brown hue of beginning acidity. On adding even two or three drops of this slightly acid solution to a beaker of a methyl orange solution, coloured an intense red by a drop or two of acetic acid, the red colour is at once replaced by the brown hue of lesser acidity.

* At the same time $\text{NH}_4\text{OH} = k' \times \text{NH}_3 \times \text{H}_2\text{O}$; the symbols are used to designate concentrations.

† The experiment may serve as a particularly simple and pretty illustration of ionic equilibrium in general, and as a basis for the discussion of the use of ammonium salts with ammonia in many important reactions of analytical chemistry, e.g., in preventing the precipitation of magnesium hydroxide and many analogous hydroxides, in facilitating the quantitative precipitation of aluminium hydroxide, &c. The simpler form is preferable for general chemistry classes, the use of the slightly alkaline ammonium chloride is more instructive for advanced students.

* Instead of using phosphorus pentabromide it was found more convenient to use the tribromide and bromine in molecular proportions, weighed in small bulbs blown at the end of capillaries. The weighing out of the exact quantities required was rapidly accomplished by weighing a bulb both on an analytical balance and on rougher scales. When by means of the latter the amount required in the bulb was very nearly adjusted, the final weighings were made on the sensitive balance, the bulb being placed in a pair of weighing tubes fitting closely over each other.

† The ordinary tubing used for heating solutions under pressure.

‡ Phosphorus trichloridibromide dissociates at 35° into phosphorus trichloride and bromine (Michaelis, *Ber. d. Chem. Ges.*, v., 9).

THE PREPARATION OF PURE TELLURIUM.*

By JAMES F. NORRIS, HENRY FAY, and D. W. EDGERLY.

(Concluded from p. 203).

Fractional Crystallisation of Potassium Bromtellurate.

Owing to the uncertainty of the homogeneity of tellurium, it was subjected to a careful fractionation. Wills (*Journ. Chem. Soc.*, xxxv., 704) fused tellurium with potassium cyanide and precipitated the element in two fractions from the aqueous solution of the telluride by a current of air. Brauner used this same process, but separated the tellurium into four fractions. He also precipitated tellurous acid in eight portions from a solution of tellurium tetrachloride, and subjected tellurium tetrabromide to fractional sublimation in a vacuum. The details of the latter method are not given.

Staudenmaier (*Zeit. Anorg. Chem.*, x., 189) crystallised telluric acid and collected the compound in four portions. In all cases atomic weight determinations of the fractions gave no evidence of a breaking down of the tellurium.

The importance of testing the hypothesis of the compound nature of tellurium led us to undertake a more careful fractionation than had been accomplished heretofore. The results of Wills, Brauner, and Staudenmaier are not conclusive, since the fractionation was not carried far enough in any case to warrant definite conclusions. Crystallisation was selected as the means of fractionation, as it appears to be much more efficient than precipitation. A number of compounds were studied with the view of using them for this purpose. The organic compounds formed by tellurium tetrachloride with anisol and phenetol, $\text{TeCl}_2(\text{C}_6\text{H}_4\text{OCH}_3)_2$, $\text{TeCl}_2(\text{C}_6\text{H}_4\text{OC}_2\text{H}_5)_2$, were prepared. They are described as crystallising well. The progress of the crystallisation could be easily watched, as the compounds have distinct melting-points. It was found extremely difficult, however, to prepare these compounds in large quantities and to re-crystallise them.

The salt finally selected was the double bromide of tellurium and potassium. This salt is readily prepared, and crystallises well from water. In order to have the results of the fractionation as conclusive as possible, all the reagents used were prepared with the greatest care.

Potassium bromide was prepared by heating chemically pure potassium bromate of commerce which had been re-crystallised four times. Hydrobromic acid was made by Squibb's method, and purified by four re-distillations from potassium bromide. The tellurium dioxide was made from basic nitrate which had been re-crystallised three times from nitric acid. The nitrate was decomposed at about 350°, and then fused in portions of 6 to 10 grms. in a platinum crucible protected by a larger porcelain crucible. Theoretical quantities of tellurium dioxide and potassium bromide were dissolved in hydrobromic acid, and the salt obtained by crystallisation. Throughout the work porcelain dishes alone were used. 800 grms. of this compound were then subjected to fractional crystallisation.

The following diagram may help to make the scheme of fractionation clear. Crystals are represented by solid lines and mother-liquors by dotted lines:—



Four portions of 200 grms. each were dissolved in water, usually containing a small amount of hydrobromic acid, and the solutions evaporated to such a point that about 100 grms. of salt separated on cooling. The salt from Fraction 1 was set aside; the salt from Fraction 2 was added to the mother-liquor of Fraction 1, making number 5; the salt from number 3 was added to the mother-liquor

from number 2; and the salt from 4 was added to mother-liquor number 3. The mother-liquor from Fraction 4 was set aside during the intermediate crystallisation of Fractions 5, 6, and 7. These solutions were evaporated as before. The salt from Fractions 1 and 5 were united, making the first portion of the second series. The mother-liquor of number 5 and the crystals from 6 made number 2 of the second series. The mother-liquor of 6 and the crystals from 7 made number 3; and, finally, the mother-liquors of 4 and 7 made number 4 of the second series. It will be seen that a complete series involves seven crystallisations. This procedure of adding the crystals of one fraction to the mother-liquor of another tends to make the most soluble and the least soluble portions collect in the end fractions. The fractionation was repeated thirty times, which involved 215 crystallisations.

There were no indications during the work of any change in the salts, so an atomic weight determination of the tellurium from the end fractions had to be made. More than fifteen different methods have been studied in attempting to determine the atomic weight of tellurium, and of these but one method—the determination of bromine in the tetrabromide—was found to give concordant results. As the use of this method is not free from objections, and involves a large amount of work, a simpler method was sought. Very concordant results were obtained in the analysis of the basic nitrate when it was changed to the oxide by ignition, and it seemed possible that trustworthy results, which would show any variation in the atomic weight, might be obtained, if the ratio between the nitrate and oxide was determined with great care.

As Klein and Morel have stated that the nitrate is hygroscopic, experiments were made with a pure sample to test this point. Two portions of the salt were heated for eight hours at 120° in platinum crucibles, transferred to a desiccator, and after cooling, were weighed immediately, a platinum crucible being used as a tare. After standing half an hour and fifteen hours in the balance case, the crucibles were weighed again, with the following results:—

Hours.	A.	B.
0	1'96242	2'19839
0'5	1'96275	2'19860
15'0	1'96274	2'19855

It will be seen that the weights remained perfectly constant after the crucibles had stood long enough to be in equilibrium with the atmosphere of the balance case, which shows conclusively that the salt is not hygroscopic. It was then heated at 120° for varying periods of time to determine whether it could be brought to constant weight.

Hours heated.	A.	B.
2'5	2'28692	2'12905
14'0	2'28667	2'12897
7'5	2'28676	2'12896
7'0	2'28672	2'12905

The above results show that this could be done very satisfactorily.

The preliminary experiments on the decomposition of the nitrate showed that the oxides of nitrogen evolved during heating carried off a small amount of tellurium dioxide mechanically. In order to avoid this loss, the following device was used:—A platinum crucible was provided with two removable platinum discs which fitted the crucible at distances of about one-half and one inch from the bottom. In the centre of the lower disc a hole was cut about one-eighth inch in diameter. The salt was placed in the crucible, the discs adjusted and the cover put on. There were three surfaces over which the issuing gases had to pass, and on these the oxide carried along was deposited. In the experiments a slight dulness was visible on the upper disc, but the cover was bright, thus showing that no oxide had reached it.

The nitrate was decomposed slowly, in order to avoid a rush of gas. It was heated for two hours at 200°, 250°, and 300°; three hours at 350°, 400°, 450°, 500°, and 550°;

* Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology. From the *American Chemical Journal*, vol. xxiii., No. 2.

and was finally fused quickly in the oxidising flame of a Bunsen burner.

The tellurium from the two end fractions of the fractional crystallisation was converted into nitrate. The salt was moistened with concentrated nitric acid when being ground, in order to prevent decomposition from atmospheric moisture. The finely-divided nitrate was heated to constant weight and converted into the oxide in the manner described above.

The results of the analysis of the nitrate prepared from the tellurium from the fraction which would contain the most soluble portion, follow:—

	$\text{Te}_2\text{O}_5(\text{OH})\text{NO}_3$.	TeO_2 .	Percentage TeO_2 .
I.	2.84426	2.37354	83.45
II.	2.55736	2.13397	83.44

The analysis of the nitrate from the fraction which would contain the least soluble portion, was made under the same conditions as before:—

	$\text{Te}_2\text{O}_5(\text{OH})\text{NO}_3$.	TeO_2 .	Percentage TeO_2 .
III.	1.39948	1.16824	83.48
IV.	1.85244	1.54649	83.49

The difference between the average of determinations I. and II., and the average of III. and IV. corresponds to a difference of 0.4 in the atomic weight. When a sample weighing 2 grms. is used, an error of 0.3 m.grm. in the weight of the nitrate would affect the atomic weight to this extent. Although the weights of the nitrate in the above experiments appear to be accurate to 0.1 m.grm., nevertheless the difference found is probably more apparent than real.

The basic nitrate is a crystalline compound and may have held mother-liquor within the crystals, although the salt was ground to a fine powder and did not lose weight when heated for ten hours at 120°. On account of this uncertainty, we do not consider the results as data which can be used for calculating the atomic weight of tellurium. The results are of value, however. The analyses of the nitrate prepared from the fractional tellurium were made under exactly the same conditions, and any error in the method would have affected the two determinations equally. We can, therefore, safely conclude that the fractionation of potassium bromtellurate did not effect any decomposition of the tellurium, which could be detected by a method capable of giving results accurate to 0.4 of a unit in the atomic weight.

The work described above is preliminary to an atomic weight determination which is now in progress. When a method has been devised which will give accurate results, the atomic weight from the end fractions will be determined, in order to decide whether the difference of 0.4 of a unit, indicated by the experiments given above, is a real one or not. We hope also to offer more conclusive evidence in regard to the elementary nature of tellurium. The fractional sublimation of tellurium dioxide, which is now in progress, seems to offer a more efficient means of deciding this point than fractional crystallisation.

This paper has been published in this unfinished form, as the departure of one of us from the Institute prevents us from continuing the work in common.

The Boiling-point of Colloidal Solutions of Salts in Water.—F. Kraft. The author has examined the retarding action to the boiling of water, of sodic or potassic soaps, palmitates, stearates, erucates, and oleates. In spite of all the precautions taken to prevent overheating (glass beads, &c.), this retardation is excessively slight; for example, only one-tenth the normal retardation, sometimes nothing at all; this arises from the colloidal nature of the salt in solution. If we then add crystalline salts, such as NaCl, we observe the increase of the boiling-point, which the latter should bring about. On the other hand, in solutions of absolute alcohol the soaps behave normally as non-dissociated crystalloids. The presence of a little water considerably increases the calculated molecular weight.—*Berichte*, xxxii., p. 1584.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

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I. INTRODUCTION.

The present investigation was taken up for the purpose of establishing the general relationships of the allotropic forms of selenium, and of determining their limits of stability. The descriptions commonly given are confusing because no systematic study of the subject has ever been made. The only available data which could lead to any conclusions are those relating to specific gravities, but these have often been determined without sufficient attention being paid to the methods by which the materials were prepared, or the conditions under which accurate results can be expected. Since none of the text-books give any adequate review of the literature dealing with this element, it is proposed to gather together here a few notes on the principal memoirs which have appeared since the discovery of selenium in 1818. This review will be strictly limited to those which deal with the properties of the element itself, neglecting those devoted to its compounds.

For convenience in discussing the earlier memoirs, the conclusions to which the present investigation has led are given below, after the list of references to the literature. Following these, there comes a description of the method of purification used, and then a discussion of the results previously recorded in the literature and those which the present experiments have brought out; these experiments include specific gravity determinations, dilatometric measurements, experiments on the behaviour of selenium in liquids, and miscellaneous observations; here follow also sections on the heat of transformation, specific heat, conductivity, &c. Finally, there will be found a section devoted to a description of the general physical properties, such as the atomic weight, vapour-density, &c., which are only inserted here for the sake of completeness.

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

† The change to selenium advocated in "Watts's Dictionary" because of the pseudo-metallic character of the element seems unnecessary; the statement made there to the effect that Berzelius so named it, is incorrect. Berzelius called it *selenium* while expressly recognising it as pseudo-metallic, between sulphur and tellurium.

II. LIST OF REFERENCES.

NOTE.—It should be noted that I have used the abbreviation "Ann." for both the *Annales de Chimie et de Physique* and *Liebig's Annalen*. Since the series number always accompanies references to the former, no ambiguity is possible.

1818. Berzelius (*Schweigg. J.*, xxiii., 309—344, 430—484).—Discovery, separation, character, compounds, atomic weight.
1826. Seebeck (*Pogg.*, vi., 155).—Electrification of vitreous selenium.
— Berzelius (*Pogg.*, vii., 242).—Purification.
— Berzelius (*Pogg.*, viii., 21).—Atomic weight.
1827. Mitscherlich and Nitzsch (*Pogg.*, ix., 627—630).—Selenic acid, and salts.
— Magnus (*Pogg.*, x., 491).—Solubility in sulphuric acid.
1828. Fischer (*Pogg.*, xii., 153—155).—Solubility in sulphuric acid.
— Magnus (*Pogg.*, xiv., 328).—Solubility in sulphuric acid.
1829. Fischer (*Pogg.*, xvi., 121).—Solubility in sulphuric acid.
1830. Magnus (*Pogg.*, xx., 165—166).—Separation from compounds.
1831. Rose (*Pogg.*, xxi., 431).—Sulphur, selenium, tellurium.
1839. Knox (*Trans. Royal Irish Acad.*, 1843, xix., 149; or *Phil. Mag.*, [3], xvi., 185).—Conductivity.
1840. Regnault (*Ann.*, [2], lxxiii., 51).—Specific heat.
— Fröbel (*Pogg.*, xlix., 590—591).—Crystal form of the metallic modification.
1845. Riess (*Pogg.*, lxiv., 50).—Electrification of vitreous selenium.
1847. Sacc (*Ann.*, [3], xxi., 119—126).—Atomic weight.
1848. Schaffgotsch (*J. Pr. Chem.*, xliii., 308—309).—Specific gravities.
1849. Erdmann and Marchand (*J. Pr. Chem.*, 1852, lv., 202).—Atomic weight.
1851. Hittorf (*Pogg.*, lxxiv., 214—220).—Melting-point of the metallic form, 217°. Transformation from vitreous to metallic causes evolution of heat. Specific gravity of metallic form. Vitreous selenium a non-conductor. Metallic selenium a conductor.
1853. Schaffgotsch (*Pogg.*, xc., 66—82).—Specific gravities.
1855. Mitscherlich (*Berl. Akad.*, 409—416; or *J. Pr. Chem.*, lxvi., 257—265; or *Ann.*, [3], xlv., 301—313).—Description of the red crystalline form, its crystallography, density, melting-point; transformation of amorphous and vitreous selenium in carbon disulphide.
1856. Regnault (*Ann.*, [3], xlv., 281—301; or *Pogg.*, xcvi., 418—434).—Specific heat, transformation, general properties, heat of transition.
1857. Oppenheim (*J. Pr. Chem.*, lxxi., 279—282).—Separation from tellurium by potassium cyanide.
— Böttger (*J. Pr. Chem.*, lxxi., 512).—Decomposition of selenide solutions.
1859. Dumas (*Ann.*, [3], lv., 186—187).—Atomic weight.
— Deville and Troost (*C. R.*, xlix., 239).—Vapour density.
1860. Uelsmann (*Ann.*, cxvi., 122).—Various compounds.
1863. Deville and Troost (*C. R.*, lvi., 891).—Vapour density.
— Werther (*J. Pr. Chem.*, lxxxviii., 180—181).—Spectrum.
1865. Böttger (*J. Pr. Chem.*, xciv., 439—440).—Separation by dissolving in sodium sulphite solution.
— Neumann (*Pogg.*, cxvii., 123).—Specific heat and specific gravity of the metallic form.
— Plücker and Hittorf (*Phil. Trans.*, clv., 1—29).—Spectrum.
1866. Schneider (*Pogg.*, cxviii., 327—334).—Solubility in selenious bromide; preparation of that substance.
1868. Bettendorf and Wüllner (*Pogg.*, cxxxiii., 293).—Specific heat of vitreous and metallic selenium. Specific gravity of the metallic form.
— Quincke (*Pogg.*, cxxxv., 629).—Capillarity constant.
1869. Fizeau (*C. R.*, lxviii., 1125).—Coefficient of expansion.
— Schultz-Sellack (*Berl. Akad. Ber.*, 745; or *Pogg.*, cxxxix., 182).—Diathermancy.
— Rathke (*J. Pr. Chem.*, cviii., 235—254 and 321—356; or, somewhat condensed, *Ann.*, clii., 181—220).—Analogies between selenium and sulphur. Various selenium compounds.
1871. Sirks (*Pogg.*, cxliii., 429—439).—Refraction and dispersion of amorphous selenium.
— Ditte (*C. R.*, lxxiii., 622).—Spectrum.
1873. Petersson (*B.*, vi., 1466—1477).—Separation by means of potassium cyanide.
— Salet (*Ann.*, [4], xxviii., 47—49).—Spectrum.
— Sale (*Proc. Roy. Soc.*, xxi., 283—285; or *Pogg.*, cli., 333—336).—Conductivity and light effect.
— Smith (*Am. J. Sci.*, [3], v., 301).—Conductivity and light effect.
1874. Rosse (*Phil. Mag.*, [4], xlvii., 161).—Conductivity and light effect.
— Rammelsberg (*Pogg.*, clii., 151—157; or *B.*, vii., 669—670).—Different modifications, crystallography, density.
— Nilson (*B.*, vii., 1719—1721).—Separation by potassium cyanide.
— Hilger (*Ann.*, clxix., 211—212).—Solubility in sulphuric acid.
1875. Siemens (*Pogg.*, clvi., 334—335).—Influence of light on conductivity (preliminary notice).
— Adams (*Proc. Roy. Soc.*, xxiii., 535—539).—Conductivity and light effect.
— Siemens (*Dingl. Pol. J.*, ccxvii., 61—63).—Electrical photometer.
1876. Petersson and Ekman (*B.*, ix., 1210—1212).—Atomic weight.
— Draper and Moss (*CHEM. NEWS*, xxxiii., 1).—Conductivity and light effect.
— Moss (*CHEM. NEWS*, xxxiii., 203).—Effect of mercury on conductivity of selenium.
— Adams (*Proc. Roy. Soc.*, xxiv., 163—164; or *Pogg.*, clix., 629—631).—Conductivity and light effect.
— Siemens (*Pogg.*, clix., 117—141; or *Berl. Akad.*)—Effect of light and heat on the conductivity of selenium.
— Adams and Day (*Proc. Roy. Soc.*, xxv., 113—117).—Conductivity and light effect.
1877. Braun (*Wied.*, i., 95).—Conductivity and light effect.
— Forssmann (*Wied.*, ii., 512—521).—Conductivity and light effect.
— Siemens (*Wied.*, ii., 534).—Conductivity and light effect.
1878. Sabine (*Phil. Mag.*, [5], v., 401—415).—Conductivity; effect of light and heat.
1879. Carnelley and Williams (*CHEM. NEWS*, xxxix., 286).—Boiling-point.
— Cross and Higgin (*J. C. S.*, xxxv., 253).—Action on water.
1880. Breguet (*Ann.*, [5], xxi., 560—563).—Photophone.
— Obach (*Nature*, xxii., 496).—Effect of phosphorescent light on conductivity.
— Bell (*Proc. Amer. Assoc. Adv. Sci.*, 115—136; or *Ann.*, [5], xxi., 399—430).—Photophone.
— Blondlot (*C. R.*, xc., 882).—Electrical properties.
1881. Kalischer (*Carl's Rep. de Phys.*, xvii., 563—570).—Photophone without battery.
— Moser (*Phil. Mag.*, [5], xii., 212).—Action between selenium and metals, &c.
— Bidwell (*CHEM. NEWS*, xliii., 105).—Telephotograph.
— Mercadier (*C. R.*, xcii., 789 and 1407).—Photophonic receivers.

1881. Spring (*Bull. Acad. Belg.*, [3], ii., 88; or *Cb.*, III., xiii., 146).—Coefficient of expansion.
— Bornträger (*Dingl. Pol. J.*, cxxlii., 55).—Preparation of metallic crystals by sublimation.
1882. Troost (*C. R.*, xciv., 1508—1510).—Boiling-point.
— Kenlen (*Bull.*, xxxvii., 440—443).—Method of extraction.
1883. Bidwell (*Phil. Mag.*, [5], xv., 31—35).—Conductivity, and heat and light effects.
— Schuller (*Wied.*, xviii., 319).—Distillation of selenium.
— Fritts (*Am. J. Sci.*, [3], xxvi., 465—472).—Conductivity and light effect.
1884. Husehus (*Journ. Russ. Phys.-Chem. Soc.*, xv., 123 and 146; or *Carl's Rep. d. Phys.*, xx., 490—499 and 565—577).—Theory of light effect.
— *Brit. Assoc. Rep.*, 440.—Spectrum.
— Bidwell (*CHEM. NEWS*, li., 261 and 310).—On the resistance of sulphur and selenium cells.
— Divers and Shimosé (*CHEM. NEWS*, li., 199).—Separation of selenium and tellurium.
1885. Schulze (*J. Pr. Chem.*, [2], xxxii., 390—407).—Soluble selenium.
— Bidwell (*Phil. Mag.*, [5], xx., 178—191).—Conductivity and light effect.
— Bidwell (*CHEM. NEWS*, lii., 191—193).—Light sensitiveness due to selenides.
— Divers and Shimosé (*B.*, xviii., 1209—1211).—Separation from tellurium by sulphuric acid.
— Morize (*C. R.*, c., 271).—Selenium actinometer.
1886. Fabre (*C. R.*, ciii., 53—55).—Heat of transformation, vitreous into metallic. (See 1887).
1887. Fabre (*Ann.*, [6], x., 472—550).—Heat of transformation.
— Bellati and Lussana (*Gazz. Chim. Ital.*, xvii., 391; *Fahresb.*, 207).—Heat conductivity of metallic selenium increased by light.
— Kalischer (*Wied.*, xxxi., 101—108).—Electromotive force and light effect.
— Muthmann (*B.*, xx., 990).—Soluble selenium.
1888. Righi (*Wied. Beibl.*, xii., 683).—Electromotive force of selenium in the light.
— Uljanin (*Wied.*, xxxiv., 241—273).—Electromotive force of selenium in the light.
— Kalischer (*Wied.*, xxxv., 397—399).—On the articles of Righi and Uljanin.
1889. Righi (*Wied.*, xxxvi., 464—465).—Reply to Kalischer.
— Korda (*J. de Phys.*, [2], viii., 231; or *Wied. Beibl.*, xiv., 50).—Conductivity.
1890. Muthmann (*Z. f. Kryst.*, xvii., 336—367).—Preparation and properties of the two monoclinic red forms. Crystallography of these and of metallic selenium.
1891. Petersen (*Zeit. Phys. Chem.*, viii., 612—616).—Allotropic forms, heat of transition, density.
— Bidwell (*Phil. Mag.*, [5], xxxi., 250—256).—Conductivity and light effect.
— Muthmann (*Zeit. Phys. Chem.*, viii., 396—397).—Isomorphism with sulphur.
— Retgers (*Zeit. Phys. Chem.*, viii., 72).—Isomorphism of sulphur, selenium, tellurium.
1893. Retgers (*Zeit. Anorg. Chem.*, iii., 343).—Solubility in methylene iodide.
1897. Tammann (*Wied.*, lxii., 280).—Two melting-points.
1898. Klages (*Chem. Zeit.*, xxii., 449—450; *Cb.*, II., ii., p. 253).—Decomposition of selenious acid by hydrogen.
— Lenher (*J. Am. C. S.*, xx., 555).—Atomic weight.

III. THE FORMS OF SELENIUM (IN BRIEF).

Selenium exists in three distinct forms:—

1. Liquid (including vitreous, amorphous, and soluble selenium).
2. Crystalline red (including perhaps two closely allied forms).
3. Crystalline grey or metallic.

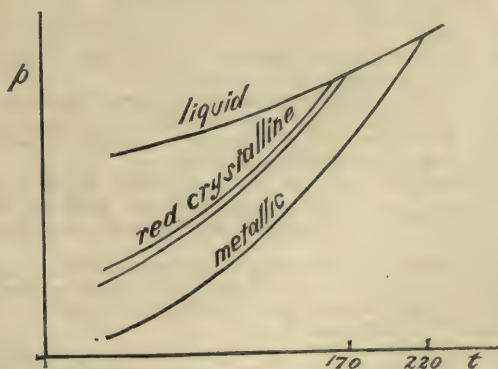
1. Liquid selenium has the properties of an ordinary liquid at temperatures above 220°. Below that it becomes gradually more and more viscous, remains soft down to about 60°, and at 30°—40° gets quite hard and brittle. In this form it is ordinarily known as vitreous selenium, from its conchoidal and brilliant fracture, and it is by that name that it will be called in the following pages. Its streak is red, and it yields on powdering at first a grey powder, but if rubbed up very fine this becomes red, and cannot then be distinguished from the form known as red powdery, or amorphous selenium, which I shall designate by the latter name. Amorphous selenium is the state in which the element separates from solutions of selenious acid on reduction; it forms, when dry, an impalpable powder without any trace of crystallinity. When warmed to 40°—50° it darkens in colour and coagulates to a soft mass, which, when cooled, becomes hard and brittle again, assuming somewhat the fracture of the vitreous form. Amorphous selenium shows all the properties of the vitreous form, making due allowance for the difference in the state of aggregation—the only difference which separates them.

Liquid selenium, whether amorphous or vitreous, is soluble to a slight extent in carbon disulphide.

Amorphous selenium, when freshly precipitated, under certain conditions, from selenious acid solutions, is soluble in water, and in this state it is known as soluble selenium. The property is lost with lapse of time.

2. The red crystalline form separates from solutions in carbon disulphide, or may be obtained by simply allowing the amorphous or vitreous form to stand in contact with that or some other solvent at ordinary temperatures. It is probable that it has two different crystal habits, both belonging to the same system, and both soluble in carbon disulphide; there may be a slight difference of stability between these two; there are indications of an instable melting-point at about 170°.

3. Grey crystalline or metallic selenium, as I propose to call it, is obtained from any of the above forms at higher temperatures; in presence of certain liquids the change takes place even at ordinary temperatures. The ease with which the transformation can be effected depends upon several factors, but the same form always results. This is the stable form of selenium, at all temperatures from the ordinary temperature to the melting-



point, 217° C. The other two forms are instable, the red crystalline one representing an intermediate stage between liquid and metallic selenium. It has not proved possible to effect a reverse transformation from the metallic into any other form below 217°, hence there is no real transition point in the physical property curves of the element.

Thus the curves representing the changes in vapour-pressure for changes in temperature should be, in their general character, somewhat as shown in the accompanying drawing (Fig. 1).

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 26th, 1900.

Dr. O. J. LODGE, F.R.S., President, in the Chair.

THE CHAIRMAN read a letter from Prof. CLEVELAND ABBE, of the United States Coast and Geodetic Survey, stating that the *Monthly Weather Review* would be sent regularly to any Member of the Physical Society expressing a wish to receive it. On the other hand, the Chief of the Weather Bureau would, at any time, be glad to receive communications referring to the Physics of the Atmosphere.

Dr. SHELFORD BIDWELL then exhibited some "*Experiments illustrating Phenomena of Vision.*" The first phenomenon illustrated was that known as "*Recurrent Vision.*" A vacuum tube, illuminated by an induction coil, was made to rotate about a horizontal axis, and was seen to be followed, at an angle of about forty degrees, by a feebly luminous reproduction of itself. A spot of white light, projected upon a screen, and caused to move slowly in a circular path, was also followed by a less luminous spot. The same effect was shown by spots of green and yellow light, but in the case of red light no ghost was visible. The phenomena of recurrent vision are due principally, if not entirely, to the action of violet nerve fibres. The next experiments related to the non achromatism of the eye. The lenses of the eye do not constitute an achromatic combination, although under ordinary conditions a bright object is not surrounded by fringes of colour. The effects of chromatic aberration are disguised by the luminous haze which surrounds the object, produced by a defect in the eye regarded as an optical instrument. A six-rayed star, formed by cutting a hole in an opaque screen, was illuminated by a gauze-covered condenser containing an incandescent lamp. The star was fairly clearly defined, and there were no fringes. More attentive observation showed a luminous haze. This haze is formed in consequence of the cellular structure of the eye, and the brightest rays—orange, yellow, and green—are chiefly instrumental in forming it. If therefore these rays are obstructed, the conditions are more favourable for the observation of chromatic aberration. The rays were consequently cut off by means of coloured glasses, and the general hue of the star was purple: to some it appeared bordered with dark blue, while to others (long-sighted) it appeared bordered with red.

Two oblong patches, one red and the other blue violet, and of approximately the same intensity, were then produced, side by side, upon a screen. An observer with very good eyesight was able, at a distance of 10 feet, to focus the patches alternately with perfect distinctness. In general, the blue patch was said to be more or less blurred. With an achromatic eye it should be possible to focus both together.

Dr. BIDWELL then showed some lantern-slides, illustrating the complex form seen when viewing a small luminous spot through a gauze-covered lens placed so as not to be in exact focus.

Some experiments were performed illustrating the principle of the colour top. When a bright image is formed on the retina after a period of darkness, it has, in general, a red border, which lasts for a fraction of a second. A dark patch, suddenly formed on a bright ground, has a blue border, which lasts for a similar time. These effects were attributed by Dr. Bidwell to a sympathetic action of the red nerve-fibres. When the various nerve fibres occupying a limited portion of the retina are stimulated by ordinary white or yellow light, the immediately surrounding red nerve-fibres are for a short period excited sympathetically, while the violet or blue and green fibres are not so excited or in a much less degree. Again, when light is suddenly cut off from a patch in a bright field, there occurs a sym-

pathetic insensitive reaction in the red fibres just outside the darkened patch, in virtue of which they cease for a moment to respond to the luminous stimulus; the green and violet fibres, by continuing to respond uninterruptedly, give rise to the sensation of a blue border. By a simple experiment it was shown that the explanation of the colour top, depending upon changes in the convexity of the eye and non-achromatism, was untenable. By the use of a strong light it is possible to get negative after-images, after looking at a brightly coloured object. These images are complimentary in colour to the object, and are formed even if the object is only viewed for a fraction of a second. By means of proper illumination and a disc rotating at the proper speed, a red wafer was so arranged that, upon looking at it, it was impossible to recognise the wafer itself, but only the continuous green after-image.

THE CHAIRMAN expressed his interest in the last experiment, in which it was possible to see the negative after-image of an object and not the object itself.

Prof. S. P. THOMPSON said these experiments threw a doubt on some of the accepted notions about the properties of the eye. Dr. Bidwell asks us to believe that the yellow haze is due to a cellular structure in the eye. Is there such a structure? can it be observed with a microscope? and do its meshes correspond in magnitude with those necessary to produce the effects? By diminishing the size of the pupil the haze is diminished, and the sharpness of the image is increased. The effects seem to be due to ordinary aberration. Prof. Thompson said that the achromatism of the eye was simply shown by covering half the object-glass of a telescope and viewing a bright object with it. The object then seems bordered with coloured fringes.

Mr. BLAKESLEY, referring to the colour patches used by Dr. Bidwell, pointed out that, although the patches were the same distance from the lens, yet they did not possess the same magnification. The last experiment shown did away with the theory of persistence of vision, because the space between the object and the negative after-image was evidently not illuminated.

Mr. TROTTER asked if red and green were the only colours which gave complimentary negative after-images.

Dr. BIDWELL, in reply, said the effect was obtainable throughout the length of the spectrum.

A paper on "*The Concentration at the Electrodes in a Solution, with special reference to the Liberation of Hydrogen by Electrolysis of a Mixture of Copper Sulphate and Sulphuric Acid,*" was read by Dr. H. J. S. SAND.

In this paper an equation has been derived for calculating the concentration at the electrode of a solution of a single salt from which the metal is being deposited under the conditions: (1) that the solution is contained in a cylindrical vessel bounded by the electrodes; (2) that no convection-currents occur; and (3) that the diffusion of the salt obeys Fick's law, and its transport values are constant. This formula can be made the basis for roughly determining diffusion coefficients. In the case of mixtures it is possible to arrive at limits for the concentration, and it has been experimentally proved that hydrogen always appears at the electrode of an acid solution of copper sulphate, in which no currents of liquid are taking place, between the limits of time for the concentration to go down to zero. The time which it takes for the hydrogen to appear can be calculated from an empirical formula, which is similar in form to the one used for a single salt. The great part played by convection-currents in determining the ratio of the two constituents given off at the electrode of an acid copper sulphate solution, has been shown by proving experimentally that artificial stirring causes hydrogen to disappear altogether in cases where it would otherwise have presented over 60 per cent of the equivalents carrying the current from the solution to the electrode.

THE CHAIRMAN drew attention to the fact that no hydrogen was liberated until all the copper had gone, and said

the formula for the concentration might be used again in further investigations.

Dr. DONNAN asked if the time at which hydrogen was liberated had been taken as the time at which hydrogen actually made its appearance in the form of bubbles, or whether any allowance had been made for saturation.

Dr. SAND said the time was taken up to the appearance of bubbles.

A paper by Dr. R. A. LEHFELDT on "*Electromotive Force and Osmotic Pressure*" was postponed until the next meeting.

The meeting then adjourned until November 9th.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 15, October 8, 1900.

Iron Silicide, SiFe_2 , and its presence in Industrial Ferro-silicons.—P. Lebeau.—The author prepares crystalline silicide of iron, SiFe_2 , by the action of copper silicide on excess of iron at a high temperature. The fused mass is treated with dilute nitric acid to completely dissolve out the cuprous compounds, when the iron silicide remains. The crystals are brilliant and have an iron-grey colour. This compound is identical with the silicide already described by M. Henri Moissan. It is only slightly attacked by acids and alkalis, with the exception of concentrated or dilute hydrochloric acid, which completely dissolves it. This compound is found in industrial ferro-silicons containing 10 to 20 per cent of silicon. To these it communicates its properties. Those compounds containing more than 15 per cent of silicon are only very slightly attacked by nitric acid, unless finely powdered.

A New Product of Tartaric Acid.—L. J. Simon.—During the calcination of tartaric acid in presence of potassium bisulphate, a new acid is produced, in addition to pyruvic and pyrotartaric, which the author succeeds in isolating. The crystals, when purified by crystallisation from hot alcohol, melt at 164° , after becoming greasy towards 158° . They re-solidify spontaneously at 156° . This new compound sublimes easily when heated to perfectly white needle shaped crystals or transparent plates. It is moderately soluble in boiling water and crystallises out on cooling. It is soluble in ether and acetic acid. The substance is a feeble acid, neutral to helianthine but acid to phthalein. The author also prepares its potassium salt, $\text{C}_7\text{H}_7\text{O}_3\text{K} \cdot 2\text{H}_2\text{O}$, the acid itself having a composition represented by $\text{C}_7\text{H}_8\text{O}_3$, and so being unsaturated. Bromine can be fixed in the cold. The potassium salt gives with silver nitrate a yellowish gelatinous precipitate, with lead acetate a white, and with copper acetate a bright green precipitate. This acid is isomeric with pyrotartaric acid, but is certainly distinct from it, and the author believes it to belong to the group of the furfurane acids.

Acetyl Derivatives of Cellulose and Oxycellulose.—Léo Vignon and F. Gerin.—Acetic anhydride, purified cotton dried at 110° , and pure dry zinc chloride, ZnCl_2 , when reacting together, give a product containing a white powder which is insoluble in water, infusible, insoluble in ether, very slightly soluble in alcohol, very soluble in acetic acid, acetone, acetic ether, and chloroform; the yield is about 25 per cent. The same operation can be repeated with oxycellulose, and there is formed, under the same conditions of acetylation, 40 per cent of the purified product, which decidedly reduces cupro-potassic solutions. A further acetylation may be performed by heating together crystallised acetic acid, purified cotton, and zinc chloride for twenty-four hours at boiling point. About 26 per cent of the product is thus obtained. These three products have

been analysed and found to be almost identical. As a result of various analyses they have been called triacetyl products, but estimation with acetic acid causes them to be classed between the tri- and the tetra-acetyl products and nearer to the latter.

MISCELLANEOUS.

University College, London.—We are requested to announce that a course of Lectures will be delivered by Dr. W. Hampson on Friday Evenings during November, December, January, and February, at 5.30 p.m. The first lecture will be delivered on November 9th. The subject of this course of lectures will be on "*Methods of Producing Artificial Cold*," and will be illustrated by experiments. Among the subjects involved will be early investigations on the condensation of volatile vapours; pressure in relation to boiling-points and freezing-points; critical temperatures; early commercial apparatus; later apparatus; intense refrigeration, with reference to the work of Pider, Caillaet, Wroblewski, Dewar, Siemens, Solvay, Hampson, and others.—There will also be a course of eight Lectures dealing with the "*Methods of Spectroscopy*," especially in connection with the Photography of the Spectrum," by Mr. E. C. C. Baly, on Friday Evenings, at 5.30 p.m., commencing on January 18th, 1901.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Assimilation of Nitrogen.—Will any reader be so kind as to give me the name of any recent publication or report bearing upon the question of assimilation of nitrogen by other plants than the Leguminosae, and by other organs than the nodules on the roots? I am convinced that these nodules are merely stores of nutriment. I have often dug up small vetches in gardens, and found, if they were extra luxuriant, that they had been growing above bits of dung put in for potatoes and other crops, and that the nodules were most abundant on the roots nearest the dung, and sometimes both above and below in close proximity to it, while they were but sparingly seen on the other roots; also, if a piece of dung was at the side of a plant, the roots on that side had nodules abundantly. The late Sir John Bennet Lawes found nodules on grasses as well as vetches.—JOHN MILNE, LL.D.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "Preliminary Examination of Applications for Patents," by W. Lloyd Wise. "The Early Manufacture of Sulphuric and Nitric Acids," by Oscar Guttman.

WEDNESDAY, 7th.—Society of Public Analysts, 8. "The Determination of the Available Brewing Extract of Malt," by Lawrence Briant. "The Definition of the Genuine Product," by C. E. Cassal, F.I.C. "Notes on certain B.P. Tests," by C. G. Moor, M.A., F.I.C., and Martin Priest.

Geological. "Additional Notes on the Drifts of the Baltic Coasts of Germany," by Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S., and the Rev. Edwin Hill, M.A., F.G.S. "On certain Altered Rocks from near Bastogne, and their Relations to others in the District," by Miss Catherine A. Raisin, D.Sc.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2137.

THE MUTUAL RELATIONS OF IRON, PHOSPHORUS, AND CARBON, WHEN TOGETHER IN CAST-IRON AND STEEL.*

By J. E. STEAD, F.I.C., F.C.S.

UNTIL quite recently the accurate study of compounds containing iron and phosphorus has had little attention. Indeed such a study was practically impossible so long as there existed no micrographic methods for distinguishing the various compounds when associated together, and of separating them from each other by chemical or other means. At the time when the subject was first attacked by the writer, nothing whatever had been published dealing with micro-structure of metals containing free phosphide of iron.

Leopold Schneider (*Österr. Zeit. für Berg- und Hüttenwesen*, xv., p. 448) had previously published results proving that, in raw irons, free phosphide of iron could be isolated by treating them with cupric chloride, the phosphide being practically insoluble in that reagent.

No one has isolated the phosphide from wrought iron and steel, or proved that it existed as such in these metals, although it is generally admitted that what phosphorus was present existed in the definite chemical compound Fe_3P .

Before describing the nature of the researches made at Middlesbrough, it will be necessary to give a brief definition of some of the terms now in use in metallographic science.

Solid Solution.

The term solid solution has been defined by Sir W. Roberts-Austen as "a homogeneous mixture of two or more substances in the solid state, and solid solutions of metals when crystalline are solid isomorphous mixtures or mixed crystals."

This definition is a most concise one, and certainly appears to cover every kind of solid solution.

As a general rule, metals and their alloys, when solid, are masses of crystals, and, when one constituent crystallises with another to form a solid solution, such a crystal, in mineralogical nomenclature, would be termed isomorphous.

Many crystals homogeneously constituted, containing two or more crystalline substances, have not exactly the same crystalline form as either of the crystal components.

Professor Bauerman, in his work on "Descriptive Mineralogy," p. 338, says that, in the strict literal sense, the term "isomorphous" is only applicable to such substances as are cubic in crystallisation as in other systems: the relation between the members of isomorphous series is one of close analogy, but not of identity."

It would appear that the term solid solution is a more suitable general term, which may be applied to crystalline or non-crystalline substances, and conveys the meaning that the bodies in solid solution are as intimately associated as if in liquid solution, and that the liquid solutions become solid solutions when they solidify. In solid solutions no microscope can detect the substance dissolved, and in that respect are identical with liquid solutions.

The term "mixed crystal," which appears to have a continental origin, may be understood, by those who use the expression, to be synonymous with isomorphous crystal.

Mixtures are, as a rule, considered to be composed of separate substances mixed up together, but not constituting a homogeneous whole. Sir W. Roberts-Austen often refers to a eutectic being a mixture, and, as the constituents of eutectics are crystalline substances, a eutectic may be called a "mixture of crystals."

In the metals containing between 16 and 21 per cent phosphorus, and 84 and 79 per cent iron, there are crystals of Fe_3P and Fe_2P placed side by side, and anyone would be justified in saying they were composed of mixed crystals.

If the term mixture in metallography is used to mean, in one case, homogeneity, and in another heterogeneity, confusion is certain to follow.

The expression "fall out of solution" is often used by metallographers, and may mean that one of the constituents of an alloy separates in advance of the remainder when the metal is passing from the liquid to the solid state, or when a constituent separates after the metal has become solid. It does not necessarily mean that the constituent falls to the bottom of the cooling mass, and disentangles itself from the fluid matrix. In most cases the constituent which falls out remains suspended in separate isolated particles, and, when the mother-liquor solidifies, are retained in that position.

If the constituent is heavier than the mother-liquor, it falls to near the bottom; if it is lighter, it rises to near the surface.

Cementite is the mineralogical term given, by Professor Howe, for carbide of iron, Fe_3C .

Pearlite or *pearlyte* is another term for the pearly constituent of annealed steels first discovered by Dr. Sorby, of Sheffield. It consists of juxtaposed bands or grains of cementite, and iron alloyed with various metals and non-metals. It contains, according to circumstances, between 0.75 per cent and 1.0 per cent carbon.

The allotropic crystals of Rosenbush are described hereafter as grains. They consist of crystal masses, which are so crowded together that the proper development of their crystalline faces and angles are interfered with.

ON THE MICROSCOPIC IDENTIFICATION OF THE PHOSPHORUS COMPOUND IN METALS.

The first object aimed at was to ascertain whether or not the phosphide isolated by chemical reagents by the Schneider process could be detected on the polished and etched sections of pig-metals containing it. With this in view, a specimen was selected which contained no chemically-combined carbon, and was what is known as glazed Cleveland pig-iron, a variety sometimes accidentally produced when an excessive proportion of coke is charged into the blast furnace with the ore. It contained nearly 5 per cent silicon and 1.5 per cent phosphorus. On polishing the surface of a section, and etching it with dilute acid and afterwards examining it under the microscope, it was found to have distributed over it small patches or areas of a brilliant white constituent closely resembling massive carbide of iron.

It was easy to see that the bright parts remained brilliant, because the nitric acid used in etching had not corroded it.

In order to isolate it, another piece of the same metal was digested with dilute nitric acid in the cold, until apparently the chemical action ceased.

The residue was filtered off, and any phosphide of iron which might be in it was attracted from it by a magnet. This was ground to fine powder in an agate mortar, and was again digested with nitric acid to remove the inclusions which escaped the preliminary treatment. The final residue, after separating magnetically and washing with alcohol and ether, contained 15.1 phosphorus.

Pure phosphide of iron, Fe_3P , contains 15.58 per cent phosphorus. It was therefore considered to be proved that the brilliant substance in the section was really phosphide of iron.

* Read before the British Association (Section B), Bradford Meeting, 1900.

Table of Heat Tints.

With steadily rising temperatures 200° to 400° C.				
0.6 p. c. P; 0.75 p. c. C.	Iron.	Carbide of iron.	Phosphide of iron.	Sulphide of manganese.
Pearlite.				
White.	White.	White.	White, tinted yellow.	Pale lavender.
Very pale yellow.	Do.	Do.	Do.	Do.
Do.	Do.	Do.	Do.	Do.
Yellow.	Very pale yellow.	Do.	Do.	Do.
Do.	Do.	Do.	Do.	Do.
Yellow-brown.	Yellow.	Very pale yellow.	Do.	Do.
Do.	Do.	Do.	Do.	Do.
Brown.	Yellow-brown.	Do.	Do.	Do.
Do.	Do.	Do.	Do.	Do.
Red-purple.	Brown.	Yellow.	Very pale yellow.	Pale yellow.
Purple.	Red-purple.	Yellow-brown.	Do.	Do.
Blue.	Purple.	Do.	Pale yellow.	Do.
Do.	Blue.	Brown.	Yellow.	Do.
Pale blue.	Do.	Do.	Salmon.	Do.
Do.	Pale blue.	Red-brown.	Heliotrope.	Brownish white.
Do.	Do.	Red-purple.	Greenish.	Do.
Pale pea-green.	Do.	Purple.	Yellow.	Do.
Do.	Pale pea-green.	Blue.	Do.	Do.
Pale yellow.	Pale yellow.	—	—	—
White.	White.	—	—	—

A series of grey metals was then prepared containing varying proportions of phosphorus ranging from 0.03 per cent to 1.5 per cent. These were polished and etched, and examined under the microscope. As was to be expected, the relative proportion of the brilliant constituent was found to diminish incidentally with the phosphorus present. On removing the marks from the slides and disarranging their order, it was easy, after examination, to re-arrange them in consecutive order. Indeed, by a little experience, it was found that, by the micro-appearance, it was possible to approximately estimate the actual proportion of phosphorus present in grey metals.

Attention was next directed to the structure of white pig-irons containing phosphorus. In such material, practically all the carbon exists in the definite chemical compound Fe_3C (carbide of iron), which, as is well known, is practically unattacked by dilute acid, so that in the etched sections both the carbide and phosphide remain bright, and cannot be distinguished from each other.

It was found, however, that carbide and phosphide of iron take different tints on heating in presence of air, and that by careful heating it was possible to get the carbide coloured a deep red-brown when the phosphide was a pale yellow. The simplest way to obtain these tints is to place the brightly polished specimen upon the surface of fluid tin maintained at a temperature of 270° to 300° C., and remove it as soon as the tint of the specimen has assumed a purple tone to the naked eye.

The accompanying table gives at a glance the progressional colouring of iron, pearlite containing 0.6 per cent phosphorus and 0.75 per cent carbon, carbide, and phosphide of iron, when heated steadily from 200° to 400° C.

If the heating is done too rapidly, the graduations do not appear in the exact order as shown.

When phosphoretic white irons were examined after proper heating, it was easy to distinguish the carbide from the phosphide.

The method of heat tinting was first used by Professors Martens and Burhens, but they did not carry their investigations far enough to enable them to use it in differentiating carbides and phosphides. M. Osmond has, however, informed the writer that he has been able to detect phosphides in pig-metals by its use, but had not published his results. It is clear, then, that the value of the method has been independently proved in France and England.

CHEMICAL METHOD FOR DETERMINING FREE PHOSPHIDE OF IRON.

The method of Schneider for separating free phosphides is objectionable, as there is much trouble in getting the

precipitated copper dissolved, and also because some of the phosphide which is in solid solution yields a decomposition product which remains insoluble together with the free phosphide.

A similar product remains on dissolving the metals in either dilute hydrochloric acid or sulphuric acid. It was, however, found that nitric acid of sp. gr. 1.20, at a temperature not exceeding 20° C., does not, to any material extent, act upon phosphide of iron in the free state, but completely dissolves all of that compound which is in solid solution.

A chemical method of determining the free phosphide was thus discovered, which, although not as accurate as could be desired, nevertheless yielded results within 5 per cent of the actual proportion present.

Having thus at command microscopical and chemical methods by which free phosphide can be detected and determined, it became practical to make a systematic research, which previously was impossible.

COMPOUNDS OF IRON AND PHOSPHORUS.

These may be divided into four classes, as follows:—

CLASS I., containing between traces and 1.75 per cent.				
" II.,	"	"	1.75 p.c.	" 10.2 "
" III.,	"	"	10.2 "	" 15.58 "
" IV.,	"	"	15.58 "	" 21.68 "

CLASS I.—Phosphorus, Traces to 1.75 per cent.

The metals of this class consist of solid solutions of phosphide of iron in iron. The phosphorus is homogeneously distributed in each, and the microscope is incapable of detecting any independent separate constituent. On treating with hydrochloric or sulphuric acid part of the phosphorus is evolved as phosphine gas, PH_3 , and part remains in a soot-like amorphous residue. The proportion evolved in the gas depends partly on the strength of the acid, but mainly on the phosphorus present. When the iron is nearly saturated with the phosphide a very small relative quantity of phosphorus as PH_3 is formed, not exceeding 5 per cent of the whole; whereas iron with under 0.10 per cent phosphorus, *ceteris paribus*, yields from 50 to 70 per cent of that element in the gaseous condition.

The results of M. Osmond, who was the first to employ this method of research, generally coincide with these observations.

It is difficult to explain why a weak solid solution should yield to acid more PH_3 than a stronger one. We know, however, that more nascent hydrogen is available in the former case, and that, as the phosphide is more attenu-

ated, it is probably more easily decomposed and hydrogenised.

The brittleness of iron increases with the phosphorus, and as the relative proportion of the phosphine PH_3 gas formed on solution of the metals in acid decreases, as a rule, with the brittleness and the proportion of phosphorus, it would not appear that a high yield of the gas can be accepted as necessarily indicative of a condition of weakness, a conclusion contrary to that of Baron Juptner. It is the main facts, however, which it is necessary should be grasped at present; the more difficult problem may be left for future research.

The black insoluble residue has a complicated constitution. It ignites spontaneously on drying at near 80°C ., and burns with a phosphoretic flame, a property probably caused by the presence of a liquid or solid hydride of phosphorus.

The ratio of iron to phosphorus does not correspond to any simple atomic proportion. It is not attracted by a magnet; it contains water, and loses considerably in weight on calcining in an inert gas.

A similar compound is left on the long continued action of dilute hydrochloric acid on phosphide of iron when the dissolving is effected with free exposure to the air; one of the facts which led to the conclusion that the black residue in both cases had a similar source, that it was derived from phosphide dissolved in solid solution in one case, and from free phosphide in the other.

The solid solutions of iron and phosphide increase in hardness with each addition of phosphorus. When iron is saturated with 1.75 per cent phosphorus, it takes a well-hardened tool to drill it.

If the phosphorus is raised above 1.75 per cent, the excess separates when the metal solidifies as a eutectic composed of phosphide of iron, and iron saturated with phosphide of iron, and is found more or less perfectly enveloping the crystalline grains, or in irregular-shaped areas inside the grains. When iron containing 1.8 per cent phosphorus is annealed by long heating at about 900°C ., and is slowly cooled from that temperature, a considerable quantity of the phosphide falls out of solid solution and appears as prismatic crystals, and the matrix then contains only about 1 per cent of phosphorus in solid solution, an observation which disposes of the conception that the compound saturated with phosphide at its solidifying point is a definite chemical compound.

The following analysis shows the changes which were effected by annealing:—

	Carbon.	Phosphorus as free Fe_3P .	Phosphorus in solution.
	Per cent.	Per cent.	Per cent.
Original ingot	0.18	0.51	1.31
After passing through malleable castings furnace ..	Trace	0.88	1.06
Portion of last metal heated to 1100°C	Trace	0.95	1.01
Portion re-melted	Trace	0.20	1.74

It is interesting to note that the more or less perfectly formed idiomorphic crystals in the annealed metal must have been formed at a temperature below the melting-point of the eutectic. In other words, that the molecular movements resulting in such a marvellous re-arrangement of the phosphide of iron and matrix must have taken place when both were in the solid state. It affords another very important link showing how closely connected are solid and liquid solutions.

CLASS II.—Phosphorus, 1.75 to 10.2 per cent.

As before stated, when the phosphorus is increased above 1.75 per cent, the metal, in solidifying, throws off the excess which appears in the cold metal as a eutectic. The proportion of this steadily increases with the phosphorus, until, when 10.2 per cent is present, the whole mass

consists of the eutectic. It may be considered to have the constitutional analysis of—

Phosphide of iron	61 per cent.
Iron saturated with phosphide in solid solution	39 "
	100 "

The melting-point is about 980°C .

CLASS III.

When the phosphorus is increased above 10.2 per cent, the excess appears at first as well-formed crystals of Fe_3P , embedded in the eutectic, and when the quantity is greater it appears in the form of grains surrounded by the same substance. When 15.58 per cent is reached, the mass is homogeneous, and consists entirely of Fe_3P .

CLASS IV.—Phosphorus between 15.58 per cent and 21.68 per cent.

When the phosphorus is increased above 15.58 per cent, somewhat porous ingots result, and, until 21.68 per cent is present, it is easy to separate the powdered metal into two distinct parts.

On endeavouring to colour or stain the constituents of polished sections so as to identify them by the usual etching methods, no success followed the effort; but on heating them till a blue oxidation temper tint was just visible to the eye, on examination under the microscope two differently coloured parts became evident, one blue, more readily oxidised than the other, and a second which appeared yellow.

Both constituents were practically homogeneous, and were evidently definite chemical compounds. One of these compounds was less soluble in nitro-hydrochloric acid than the other. The more insoluble part was least readily attracted by the magnet.

The constituent readily coloured blue by heating was the more soluble in acid, and was strongly attracted by the magnet. It consisted of Fe_3P .

The more insoluble compound, Fe_2P , separated by acid, contained—

Iron	78.30 per cent.
Phosphorus	21.50 "
Not determined	0.20 "
	100.00

The compound of iron and phosphorus containing about 18 per cent phosphorus, which had about equal parts of Fe_3P and Fe_2P , was most fragile and very porous, and the crystals loosely attached to each other were easily separated by slight pressure. On placing the coarse crystalline matter on a steel plate, and heating it till some of the particles took a "temper blue colour," and then rapidly cooling the whole, it was easy to pick out the blue particles from those of a pale yellow colour. On testing them chemically side by side, the blue particles were found to approximate to the composition of Fe_3P , the yellow crystals to Fe_2P .

When the mixed mass of blue and yellow particles was approached by a magnet to within a distance of 2 m.m., the blue particles were attracted and adhered to the magnet, the yellow ones remaining behind.

The analyses of the magnetically separated compounds were as follows:—

	Magnetic.	Slightly magnetic.
Iron	84.00 per cent.	78.40 per cent.
Phosphorus	15.82 "	21.50 "
Not determined	0.18 "	0.10 "
	100.00	100.00
Corresponding to the formula of	Fe_3P	Fe_2P .

(To be continued).

THE ESTIMATION OF TUNGSTEN IN STEEL AND STEEL-MAKING ALLOYS.

By FRED. IBBOTSON and HARRY BREARLEY.

THE common way of separating tungsten from the solution of the steel in nitric, nitro-hydrochloric, or nitro-sulphuric acid is to evaporate to dryness, take up in HCl, and filter off the WO_3 at once, or after re-evaporating once or twice more. The avowed object of the re-evaporations is to ensure the complete separation of the tungstic oxide, some of which, with only one or two evaporations, is liable to remain dissolved in the HCl solution. These instructions are based on the very common assumption that the tungstic acid precipitated by the first evaporation remains as a precipitate while the second evaporation is being made. This, however, is not so; unless tungstic oxide has been ignited at redness, it is very appreciably soluble in hydrochloric acid, so that after evaporating any number of times the final "take up" in HCl always takes up also many times more WO_3 than was supposed to be unprecipitated at the first evaporation, and this is only re-precipitated after evaporating to low bulk or at once diluting with water. Tungstic oxide is hardly, if at all, soluble in HCl diluted with two or three times its volume of water.

Of the other processes adopted for separating the tungsten from the iron, the only ones much in use, which are not in some way modifications of those indicated above, are—

1. *Separation with Copper Solutions.*—In which case the residue may contain other non-combustible bodies besides tungsten, the most objectionable of which is chromium; and
2. *Solution in Acids and Fusion with Na_2CO_3 of the Dried Residue.*—In this case also chromium accompanies the tungsten. Even when the WO_3 is separated by evaporation with acids, it is occasionally contaminated with chromium.

Any of the above processes, when the WO_3 is freed from SiO_2 and Fe_2O_3 (traces) merely, or fused and re-precipitated as mercurous tungstate, give satisfactory results with pure carbon tungsten steels; the extreme results of estimations made on the same steel in seven different ways being 4.32 and 4.46 per cent tungsten.

The following process is submitted not as a rigidly accurate one; the results are always about 0.05 per cent too low. It is, however, more rapid than any other method we know, and—either with or without a correction—the results are good enough for technical purposes. The course of the reactions are most clearly seen when applied to a ferro-alloy containing very little carbon.

Digest the powdered alloy or steel borings with strong HCl (about 100 c.c. for 5 grms. of steel) short of boiling; the iron is easily attacked, but the W is not. On adding only a few drops of nitric acid the ferrous changes to ferric chloride, and then the W becomes visibly attacked until the clear orange-coloured ferric chloride blackens again, showing that some ferrous chloride has been formed. By a repetition of these changes, using only rather more nitric acid than is needed to keep the iron wholly in the ferric state, the sample all passes into solution in a few minutes. This may appear contrary to the experience of those who have frequently decomposed tungsten steels and alloys with aqua regia, and noticed that tungstic oxide—usually brown and not pure— invariably separates; but the explanation is to be found in the use of enough HCl to completely dissolve all the WO_3 , and no more HNO_3 —which decreases the solubility of WO_3 in HCl—than is necessary to effect the oxidation. If, now, the acid solution of the metal be boiled until WO_3 just begins to separate, then diluted with at least twice its volume of water and boiled, all the WO_3 except 2 or 3 m.grms. is precipitated. The ignited precipitate contains usually the bulk of the silica, which is driven off with HF, and traces of Fe_2O_3 , which may be allowed for

after fusing with Na_2CO_3 , filtering, and estimating the Fe by re-ignition and weighing. The essential points are:—To have enough HCl present, in as strong a form as possible, to hold the WO_3 in solution; to keep the temperature below boiling-point, so as not to weaken the HCl; and, after everything has dissolved, to have as little HCl as is practicable over and above that needed to keep the WO_3 in solution. The process can obviously only be tested on actual steels. The following results (uncorrected) were obtained:—

TABLE I.—Percentage Tungsten.

New process.	Standard process.
4.36	4.38
2.91	2.95
3.49	3.54
2.99	3.02
8.68	8.70
6.93	7.00

The last two samples contained 2.25 per cent chromium. After fusing with Na_2CO_3 to separate the small amounts of iron, the filtrates were observed to have a faint yellow tint. This was allowed for by acidifying, titrating with $FeSO_4$ and $KMnO_4$, and calculating the amount of Cr_2O_3 to be deducted. We have never found as much as 1 m.grm. Cr_2O_3 along with the tungstic acid.

Ferro tungsten Alloys.—These alloys may contain from 15 to 80 per cent of tungsten. They are incompletely soluble in 1:20 HNO_3 and in nitro-hydrochloric acid as it is usually applied. The decomposition is both rapid and perfect when the powder, preferably agate ground, is treated with HCl and a minimum of HNO_3 in the manner already indicated. One grm. of a 50 per cent alloy can be completely dissolved by using 50 c.c. HCl; when the W is higher, rather more, when lower, rather less HCl is needed. As the amount of material which can be conveniently handled is, at most, but 2 grms., the small quantity of WO_3 which is not precipitated on diluting the dissolved sample with water cannot be overlooked. By evaporating the filtrate from a number of ferro-tungstens, we have found that about 1 per cent of the total tungsten present generally remains dissolved.*

When an empirical correction of this kind cannot be tolerated, and a more complete analysis is desirable, the dissolved sample is evaporated in the water-bath, boiled with HCl which has been diluted three or four times, and the $WO_3 + SiO_2$ filtered off. This alternative is longer, but more accurate and less troublesome because it demands little or no attention, and the WO_3 is in a more easily filtered state; and, further, the small amount of Mo which is usually present will have completely passed into solution.

Self-hard alloys, which are ferro-tungstens containing considerable amounts of chromium, silicon, and manganese, are readily attacked by HCl and a little HNO_3 . Column 4 in Table III. represents the analysis of an alloy which is sold, along with the following instructions, for the making of self-hard steels:—"One-third alloy melted with two-thirds Swedish Bessemer."

Nickel-tungsten Alloys.—This alloy should not be opened up by fusion with soda carbonate. If finely powdered, it is attacked by fusion, but it is necessary to examine the undissolved oxide for tungsten. This method has also the disadvantage of separating chromium, which occasionally occurs in small quantity in these alloys along with the tungsten.

It is very easy to dissolve the powdered alloy in a mixture of hydrofluoric and nitric acids. The efficiency of both this mixture and the HCl with a little HNO_3 depends on the solubility of WO_3 in HF or HCl, but as WO_3 is more soluble in the former, a much less volume of it is needed. To the dissolved sample, from which the nickel

* In some cases, after standing all night, hardly a trace of WO_3 can be found by evaporating the filtrate.

has a strong tendency to separate in well-formed green crystals, add H_2SO_4 , evaporate to strong SO_3 fumes, dilute, filter off WO_3 , and weigh. The nickel in the filtrate—separated from iron or not as occasion demands—is estimated cyanometrically. A rapid estimation of the Ni, if only small amounts of iron are present, may be accurately made by dissolving as before, pouring at once into an excess of ammonia, and titrating a portion of the filtrate for Ni.

The use of HF for dissolving the sample prevents Si being estimated; it also causes a portion of the molybdenum to be volatilised. The more complete examination is carried out by dissolving (as for ferro-tungsten), evaporating, separating the $\text{WO}_3 + \text{SiO}_2$, and estimating Mo as PbMoO_4 , and nickel with KCN and AgI.

The Analysis of Tungsten-molybdenum Steels.—Tungsten can be separated from iron by pouring the solution into an excess of caustic soda, just as Mo and Fe are separated (CHEMICAL NEWS, lxxi., 269), but the former separation is not nearly so easily made as the latter. It can be made, however, with perfect accuracy when test solution, made by adding standardised Na_2WO_4 to a ferric solution is poured into a considerable excess of vigorously agitated soda hydrate. But the nitric acid solution of an actual steel cannot be so easily resolved, although it is desirable that it should be, in order that the molybdenum and tungsten might be precipitated together as lead salts and separated in the manner described in a former paper (CHEMICAL NEWS, vol. lxxi., p. 13). No doubt the separation of the Mo and W from the iron will be made in this way ultimately, but at present we find the following process to be more reliable and expeditious:—

Dissolve 2 to 5 grms. of the sample in the manner previously described in connection with W steels, evaporate to pastiness or to dryness, but do not bake, boil with dilute HCl (three or four to one), filter off WO_3 , and estimate Mo in the filtrate by separating the iron with NaHO and precipitating the Mo as PbMoO_4 . The process was tested by making duplicate analyses of tungsten-molybdenum steels, by assaying mixtures of tungsten and molybdenum steels, and W steels mixed with fused metallic Mo. The results obtained were:—

TABLE II.

Percentage present.		Percentage found.	
Mo.	W.	Mo.	W.
1.16	4.50	1.18	4.51
2.51	4.50	2.54	4.47
5.67	4.50	5.70	4.51
1.41	4.38	1.40	4.38
Duplicate assays of		1.76	1.82
Mo-W steel ..		1.78	1.84

The Analysis of Tungsten Powders.—The points to which our attention has been directed in the examination of these powders are:—The estimation of W, Na_2WO_4 , WO_3 , Mo or Mo compounds, Si or SiO_2 , Fe and Fe oxides, Al_2O_3 and CaO. The last two compounds occur more frequently and in larger amount than is commonly suspected.

Another constituent of these powders which has not, to our knowledge, been previously mentioned, and which, up to the present, we have no reliable means of estimating, induces us to defer what observations we have to make on the general analysis of these powders. This strange component exists as cubes and tetrahedra with colours varying from bright bronze to brown. In the purest form in which it has been isolated from the W powder, it has a specific gravity of 7.3. In physical properties therefore it corresponds to tungsten-bronze; and such of its chemical properties as we have determined favour the same conclusion. It need only be assumed that the alkali of the tungstate which is decomposed to provide the WO_3 for reduction to W is not washed completely away in order to provide, in the manufacture of the tungsten powder,

just such circumstances as are favourable to the production of tungsten-bronze.

The occurrence of these red crystals has been observed in each of twenty samples, taken promiscuously from British, German, and French supplies when examined in the following manner:—Boil with a dilute solution of NaHO in a basin, stir well, and pour the liquid off. By virtue of their lesser specific gravity, the coloured crystals lie on the surface near to the lip of the basin. A commercial sample made in this district contains nearly 20 per cent of these crystals. They are isolated by passing the powder on to a sieve of 60 meshes to the lineal inch; this retains 50 to 70 per cent of the impure crystals. These are boiled with NaHO, and washed so as to remove adherent powder. After drying, they are digested with nitrofluoric acid, which dissolves practically all the metallic tungsten, and also a portion of the crystals. The residue is washed and boiled with NaHO; the resulting highly-coloured crystals have the aforesaid specific gravity.

We should be very pleased to hear from anyone who, having previously noticed these crystals, has identified them and knows how they may be accurately estimated.

The following are analyses of commercial tungsten alloys:—

TABLE III.

	Fe-W.	Ni-W.	Self hard.	W powder.
W	55.20	72.89	25.78	95.43
Mo	0.23	traces	—	0.16
Ni	—	22.96	—	—
Fe	42.59	1.26	55.99	0.22
Cr	—	—	2.90	—
Si	0.40	0.84	0.59	—
SiO_2 ..	—	—	—	0.40
C	1.09	1.32	4.64	0.05
Al_2O_3 ..	—	—	—	1.38
Mn	0.26	0.29	10.12	traces
S	0.165	0.275	—	—
Na_2WO_4 ..	—	—	—	1.25
WO_2 ..	—	—	—	0.67
Red crystals	—	—	—	Present, but not estimated.
	99.935	99.835	100.02	99.56

The Technical Department,
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THE REDUCTION OF TUNGSTIC ANHYDRIDE BY ZINC: THE PREPARATION OF PURE TUNGSTEN.

By MARCEL DELÉPINE.

FROM the calorimetric measurements made by M. Hallopeau and myself (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 945) on the heat of oxidation of tungsten, it was easy to devise a method for the preparation of this metal; if its heat of oxidation is correct, all metals with a greater heat of oxidation would be able to remove it from its oxides in the same manner as it displaces from their oxides all the metals with a lower heat of oxidation.

Apart from the experiments made by M. Moissan (*Comptes Rendus*, 1896, vol. cxxiii., p. 13), which require a great deal of attention in order that the reduction of the tungstic anhydride by the carbon in the electric furnace may be stopped exactly at the phase when the metal is integrally decarburised, there exists up to the present time no process by which large quantities of pure tungsten can be prepared. The reduction of WO_3 by aluminium, according to M. Goldschmidt's process, even with the modifications introduced by M. Stavenhagen, gives the melted metal, but this latter is liable to contain aluminium (*Berichte*, vol. xxxii., p. 1513).

By the method I propose to use, I reduce tungstic anhydride by means of zinc, a common metal which adds a practical interest to the theoretical one, which is by no means to be disdained.

According to thermochemical data we have :—



As a matter of fact I have effected this reaction with : 1) pure zinc and pure tungstic anhydride; (2) pure zinc and pure tungstate of ammonium; (3) commercial zinc and tungstate of ammonium made from commercial tungstic anhydride; and (4) commercial zinc and tungstic anhydride such as is extracted directly from wolfram by Woehler's method.

It is sufficient to heat the mixture of WO_3 with 1.5 parts of powdered zinc to a red heat over a fire made of wood charcoal, coke, or gas, until the zinc no longer distills over; in all cases we obtain a black, very friable mass, consisting of tungsten, oxide of zinc, and a little tungstic anhydride, or a lower oxide, resulting from an incomplete reaction.

This mass should be treated in the following manner. The oxide of zinc formed is removed by hydrochloric acid, then wash till the acidity has been removed; this gives a product containing 98.5 per cent of W, or about 94 per cent of the metal, and 6 per cent of WO_3 . Boiling the black powder obtained, with soda for a few minutes, then washing until the alkalinity is removed, almost completely eliminates the oxides, and, according to the care with which the operation has been carried out, gives a metal of 99.5 to 100 per cent purity. In any case, the metal heated to redness for an hour in a current of hydrogen will always give a product of 99.8—99.9—100 per cent of purity. This operation can be carried out on quantities of two hundredweight at a time, which is impossible when starting from tungstic anhydride.

The following analytical results show the degree of purity of the products formed by the different methods of preparation mentioned above; 100 parts contain in tungsten :—

	After washing with HCl.	After using NaHO.	After the action of H.
1.	98.6	99.65, 99.44, 99.48	99.92, 99.89
2.	98.5	—	99.80, 99.93
3.	—	99.88, 100.00	—
4.	98.62	—	99.98, 99.90, 100.0

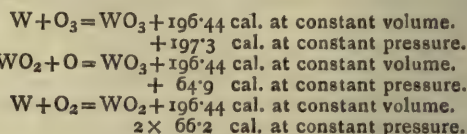
We see that the purity of the zinc has no influence on the quality of the product, which shows that these impurities were either volatile or soluble in the alkali. It must, however, be noticed that products 2 and 3 prepared from ammoniacal salts may possibly contain a thousandth part of nitrogen eliminable by means of the melted alkalis in the form of ammonia.

The metal obtained by this zinc process is a greyish-black dense powder, taking a metallic lustre on being subjected to great pressure or on trituration in a mortar, burning in the air with great facility, while becoming entirely changed into yellow tungstic anhydride. With other reagents it also shows considerable chemical activity, which, however, is only due to its fine state of division. Most of the above analyses were made by burning the metal placed in a heated crucible in the air; the oxide formed is completely soluble in melted carbonate of soda. By estimations with mercurous nitrate I recovered, to within 1/800th part, the WO_3 existing after the oxidation in the air. This slight loss may easily be attributed to losses of manipulation; the simple oxidation in the air constitutes, in fact, a very exact method of estimation.

The density of samples 2 and 4 was found to be respectively 18.67 and 18.61, figures which are very close to those given by M. Hallopeau for crystallised tungsten (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 997), and by M. Moissan for melted tungsten (*loc. cit.*).

Finally, the finely-divided pure metal which I now possessed in large quantities enabled me to determine

afresh, and under more stringent conditions, the heat of oxidation of W to WO_3 . By operating on about 2 grms. I found for 1 grm. 1064.0 cal., 1071.5 cal., and 1067.2 cal., a mean of 1067.6 cal., or almost indently the same value that had been previously found, but certainly more exact. I, therefore, definitely put forward the following figures :—



These figures, so close to those for iron, suggest another question. Is it really necessary to heat to such high temperatures as those recommended by Deville, Riche, and Dumas to reduce tungstic anhydride by hydrogen? No. I have observed that tungstic anhydride heated in a porcelain boat in a glass tube loses all its oxygen in from one to two hours under the influence of dry hydrogen, and that at only a red heat considerably below the softening point of glass; the loss of weight is found to be equal to the increase of weight on oxidation.

To sum up, the reduction of tungstic anhydride, either by hydrogen or by zinc, easily enables us to obtain pure tungsten, and that in as large quantities as we wish, and by the use of zinc at temperatures very little above the distilling point of this metal. Apart from its pulverulent physical state, the metal thus prepared has the density and the heat of combustion of tungsten, either crystallised or melted; it can also, by compression or trituration, assume the brilliant lustre of a metal, so that we are perfectly justified in stating that it is in the same condition, its finely-divided state being only due to the want of fusibility of the metal.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 16, p. 675.

THE DETECTION OF IODIC ACID IN THE PRESENCE OF CHLORIC, BROMIC, PERCHLORIC, AND PERIODIC ACIDS, BY MEANS OF SULPHATE OF MORPHINE.

By C. REICHARD.

WHEN we treat an iodate, such as iodate of potassium, in aqueous solution, with a solution of sulphate of morphine and a few drops of sulphuric acid, we obtain a brown precipitate if we use a concentrated solution. If we have to deal with dilute solutions, a brownish colouration or a yellowish-brown or yellow precipitate is formed, according to the amount of iodic acid present. The reaction is more especially sensitive if, after adding the reagent, we drop a small quantity of ammonia into the mixture.

Sulphate of morphine enables us to detect the least trace of iodic acid, even in the presence of chloric, bromic, and perchloric acids, on which this reagent has no action. As for periodic acid and the periodates, the action is not the same, and we offer the following remarks on the subject. Periodate of potassium is very slightly soluble in water (100 parts of cold water dissolve 0.3448 part of KIO_4), and the aqueous solution treated with sulphuric acid remains colourless; but when treated with sulphate of morphine it almost immediately acquires a yellow colouration, and this phenomenon takes place as well with concentrated solutions as with dilute ones. After standing for a more or less prolonged period this colouration disappears, exactly as with iodate of potassium; but when we add a slight excess of dilute ammonia to either concentrated or dilute solutions of the periodate, there is, in both cases, a more or less pronounced colouration, but when left to themselves for a time at the ordinary temperature the two solutions behave differently. While

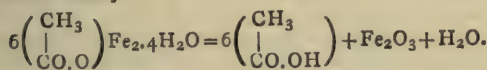
the dilute solution keeps its original brownish-yellow tint, even after several days, the concentrated solution becomes almost colourless after only twelve hours. The colour of this latter is brought back by ammonia, but it is then much less pronounced. The dilute ammoniacal solution, even when boiled, retains its colouration.

Solid iodate of potassium, treated with sulphuric acid and morphine, gives a solid brown precipitate of free iodine, while under the same conditions the periodate only gives a yellow solution. The very slight solubility of the periodate, compared with the great solubility of the iodate, enables us to separate these two iodic acids by means of successive additions of small quantities of cold water. In this manner we finally obtain a residue of pure periodate which can be easily recognised.—*Chemiker Zeitung*, 1900, p. 644.

A METHOD FOR THE ESTIMATION OF ACETIC ACID.

By V. DELFINO and M. MIRANDA.

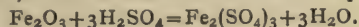
WHEN we add an excess of a concentrated solution of ferric chloride to acetic acid (vinegar should be first decolourised by means of animal charcoal), a deep red colour is produced. This colouration is destroyed by heat; a gelatinous mass is then formed, which almost immediately resolves itself into hydrated ferric oxide, while acetic acid is set at liberty:—



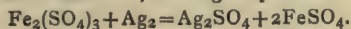
(Marignac's formula).

When submitted to the action of heat the hydrated ferric oxide is transformed into anhydrous ferric oxide, which adheres to the sides of the beaker or flask in which the operation has been performed. It is then only necessary to determine the weight of the anhydrous oxide and to multiply the quantity of metallic iron obtained by the factor 3.2143 to get the quantity of acetic acid.

It is, however, simpler to estimate the metallic iron directly, and the following is the method we adopted:—The ferric oxide is treated with hot concentrated sulphuric acid, which transforms it into ferric sulphate,—



This solution is diluted, and a strip of silver is plunged into it. On applying heat, the silver causes the ferric sulphate to pass into the ferrous state, and at the same time it is itself dissolved, forming sulphate of silver,—



Care must, however, be taken not to allow the solution to cool, or else the sulphate of silver will be precipitated in the crystalline form and the ferric sulphate regenerated. After making sure that the reduction of the ferric salt is complete, we add an excess of hydrochloric acid to the solution to precipitate the silver in the state of chloride, which may then be separated by filtration. Under these conditions there is no longer any danger in allowing the filtered solution to cool, and the iron may then be estimated volumetrically by means of permanganate of potassium.—*Moniteur Scientifique*, Series 4, vol. xiv., October, 1900.

Royal Institution.—The Annual Course of Christmas Lectures, specially adapted to Young People, at the Royal Institution, will be delivered by Sir Robert S. Ball, F.R.S., Lowndean Professor of Astronomy in the University of Cambridge, whose subject is "Great Chapters in the Book of Nature." The first lecture will take place on Thursday, December 27, at Three o'clock, and the remaining lectures will be delivered on December 29, 1900, and on January 1, 3, 5, and 8, 1901.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 217).

IV. PURIFICATION OF THE MATERIAL.

It was not essential for the present investigation that the last traces of impurity should be removed; hence no attempt was made to prepare absolutely pure selenium. The substance in its original form contained a considerable quantity of sulphur and a very little tellurium as impurities. The method used was to dissolve by heating in concentrated sulphuric acid, thus oxidising the selenium to selenious acid, and then to precipitate by means of sulphur dioxide. Before precipitating, the sulphuric acid solution was diluted with water, and, if necessary filtered.

Divers and Shimosé (1884) found that this method of purification was effective in removing the tellurium which does not come down under these conditions, but may afterwards be precipitated by the addition of hydrochloric acid.

After reduction, vigorous shaking is necessary to bring the material together, and it should then be washed until the washings show no further acidity. If the red selenium be then separated on the filter, it will be found very difficult to dry; standing for weeks in a desiccator over sulphuric acid will not free it from water; it is therefore better to make a final washing with alcohol, then filter and dry in the air on a porous porcelain plate. One gram. of the material thus purified, when dissolved in nitric acid and diluted, gave no appreciable indications of the presence of tellurium, and a test for sulphur showed that this element also was present in only very small quantity.

V. THE PROPERTIES AND TRANSFORMATIONS OF THE DIFFERENT FORMS OF SELENIUM.

1. The Vitreous Modification.

The form in which the element comes into commerce is the one known as vitreous, from its brilliant conchoidal fracture. The commercial material in former years consisted of medallions bearing the image of Berzelius, the discoverer of the element, but it is now almost always supplied in rods. Its colour in the mass is black, but thin fragments are translucent, and display a deep ruby-red colour, and when very finely powdered the powder is red. When heated it begins to soften at about 50°, and if the heating is extremely rapid it is possible to raise the temperature to 220° without causing any transformation into a denser form; at this temperature it is distinctly liquid, though still viscous; it does not attain a state of thin fluidity below about 250°. This has led to a misleading statement in many of the text-books, the responsibility for which rests with Sacc (1847) to the effect that, while the grey crystalline or metallic variety melts sharply at 217°, the vitreous form only becomes really liquid at 240°–250°. The fact, of course, is that the liquid obtained at 217° is the same from whichever source, but it possesses at that temperature a moderately high viscosity. When melted selenium is cooled down the vitreous form is always obtained, unless the cooling is conducted very slowly, in which case it may go over to the more stable metallic form.

Berzelius (1818) remarks that the vitreous form is semi-fluid at 100°, completely so a few degrees higher; probably in his experiment the transformation into the metallic form set in at about the time that the temperature had attained 100°; this change sets free so large a quantity of heat that the mass may very well have assumed for a few moments a state of thin fluidity.

If vitreous selenium be slowly heated and a thermometer placed in the mass, it is found (Regnault, 1856) that when the temperature has attained a point about 96°–97° there

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

is a sudden rise in the temperature, amounting under favourable circumstances to as much as 150° ; the mass becomes completely fluid, and after a few moments hardens again. The substance thus formed is found, when examined, to possess quite different properties from the original vitreous selenium. This is, in fact, the grey crystalline form, appropriately called by Regnault metallic selenium.

This transformation was studied by Hittorf (1851), later by Regnault and many others. Regnault's observation that the change begins at 96° — 97° has led to the belief that there is something significant in these temperatures. Such is not the case. The fact is that vitreous selenium probably goes over into the metallic form at all temperatures under 217° , but the change, in the absence of solvents does not possess a measurable velocity below about 90° . Indeed, Regnault states that it may be kept for hours at 90° without any change occurring. This is probably true, in general, when selenium is heated by itself; nevertheless, Hittorf states that the change occurs anywhere between 80° and 217° , and Rammelsberg (1876) gives 90° as the limit of stability. At 95° , or any higher temperature, until we approach the melting-point, the change goes on rapidly. Hittorf made some experiments to determine the point of maximum velocity, and placed it at about 125° .

Positive evidence was still wanting to show whether the change was really a reversible or an irreversible one, i.e., to determine whether vitreous selenium is really unstable at all points below 217° , or whether it has at lower temperatures a region of stability. The idea of a transition point has gained a hold on the minds of some, through a remarkable experiment of Lehmann, which we shall now consider. Thus Tammann (1897) has been led to consider this an example of a substance having a second melting-point, analogous to the case of chloroform as reported by Piéet (*Zeit. Phys. Chem.*, 1895, xvi., 422). Further, Le Chatelier, in a more recent article (*Comptes Rendus*, 1899, cxxix., 282), expresses himself in these words: "Selenium is only stable in the crystalline state above 60° and below 214° . Outside of these extreme limits of temperature, the amorphous modification (vitreous, liquid) alone is stable."

The observation of Lehmann upon which these statements are based, was made with the microscope, and is reported by him as follows ("Molekularphysik," i., 712):—

"When melted under a cover-glass, selenium appears as a clear red transparent liquid; on further warming, the liquid gets darker and black points make their appearance here and there; these increase in size and assume the aspect of spherical aggregates (sphärolithische Aggregationen) of the insoluble grey modification. . . . The crystals soon fill the whole field, and, on still further heating, the mass melts to a dark almost opaque liquid. On cooling down slowly, the spherical crystals of the grey modification appear at first, and then, as they grow steadily smaller, the colour of the liquid becomes less intense, and we obtain, finally, the original clear red liquid. If the cooling is rapid, the crystals of the grey modification do not appear, but the liquid passes gradually from dark red to light red. The same behaviour is shown on rapid warming; here also the black crystals may appear momentarily and disappear again, but sometimes the transition is direct from the red condition into the more deeply coloured one. The increased absorption of light on heating and the reverse change on cooling, point to a chemical change in the liquid such that it is to be regarded at higher temperatures as partially a solution of the grey modification.

On attempting later to reproduce the above inversion (Rückgängigwerden der Entglasung) it did not prove possible to do so; perhaps because of greater or less impurity of the selenium, perhaps because the conditions were not favourable for the production of the grey (light-sensitive, less conducting) modification." All my attempts to repeat this observation of Lehmann's also failed. I have not been able to find under the microscope anything abnormal

in the behaviour of the element. Lehmann's observation must therefore remain for the present unexplained; possibly local heating or some other experimental irregularity may have been the cause of the appearance and subsequent disappearance, at lower temperatures, of the crystals.

A better method of approaching this problem is afforded by measurements with the dilatometer, and the following section is devoted to an account of such experiments.

Dilatometer Measurements.

The experiment of Lehmann, to which reference is made above, indicated the possibility of a real transition-point in the change from vitreous to metallic selenium. Dilatometric measurements being the most satisfactory means of establishing such a point, the present study was begun with the dilatometer. The difficulties met with, which are discussed later on, had their source in the fact that it was necessary to work over a range of more than 200° , and it was not easy to find a liquid which answered the purpose. Several were tried—*aniline*, *quinoline*, *glycerin*, and solid and liquid *paraffin*.

For those determinations which were made with solid paraffin, it was necessary to surround the stem of the dilatometer with a steam jacket, and also to enclose that part of it which passed through the lower stopper of the jacket, in copper tubing, to prevent the solidification of the paraffin in the capillary.

Even when liquid paraffin is used, the steam jacket is of value because, without it, the high viscosity of the paraffin at lower temperatures renders it difficult to obtain concordant results where the bulb is subjected to rapid changes through a wide range of temperature.

For the sunlight experiments, a bath of glycerin or high-boiling paraffin was used; for the others, a bath of oil. The Reichert gas regulator proved of service in maintaining a constant temperature within a couple of degrees, when it was desired to keep the bath for some time at a fixed point. The stirring was done by means of an electric motor; what is known as the Ajax motor proved most efficient. The dilatometer tube was always sealed; hence the pressure was generally higher than one atmosphere for the upper ranges of temperature. The recorded experiments are given under their original numbers, so that the series as given here is not complete.

(To be continued).

THE TITRATION OF MERCURY BY SODIUM THIOSULPHATE.*

By JOHN T. NORTON, Jun.

ACCORDING to J. J. Scherer ("Lehrbuch der Chemie," i., 513) mercurous nitrate, mercuric nitrate, and mercuric chloride may be estimated by direct titration with sodium thiosulphate, $\text{Hg}_2\text{S}_2\text{HgS} \cdot \text{Hg}(\text{NO}_2)_2$, and $2\text{HgS} \cdot \text{HgCl}_2$, being the precipitates obtained in each case. I have been unable to obtain access to Scherer's original publication, but Sutton ("Volumetric Analysis," p. 220) gives the following very general directions for this process:—

(a) "*Mercurous Salts*. The solution containing the metal as a protosalt only is diluted, gently heated, and the thiosulphate delivered in from the burette at intervals, meanwhile well shaking until the last drop produces no brown colour. The sulphide settles freely, and allows the end of the reaction to be easily seen. One c.m.³ of the 1/20 normal solution of thiosulphate = 0.02 grm. Hg or 0.0208 HgO.

(b) "*Mercuric Nitrate*.—The solution is considerably diluted, put into a stoppered flask, nitric acid added, and

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1900, vol. x., No. 55.

TABLE I.

	HgCl ₂ taken, calculated as Hg.	Na ₂ S ₂ O ₃ in excess.	Volume at beginning.	HgCl ₂ found, calculated as Hg.	Error.
	Grm.	C.m.s.	C.m.s.	Grm.	Grm.
1.	0.0446	46.28	200	0.0343	0.0103 -
2.	0.0354	46.28	400	0.0326	0.0028 -
3.	0.0356	44.97	400	0.0225	0.0131 -
4.	0.0345	44.5	100	0.0308	0.0037 -
5.	0.0154	44.43	50	0.0326	0.0028 -
6.	0.0382	22.59	50	0.0354	0.0028 -
7.	0.0375	8.58	50	0.0385	0.0010 +
8.	0.0371	1.84	50	0.0304	0.0067 -
9.	0.0731	2.28	50	0.0774	0.0043 +
10.	0.1486	9.34	50	0.1489	0.0003 +

TABLE II.

	HgCl ₂ taken as Hg.	Volume at be- ginning.	Temp.	Stand- ing.	Na ₂ S ₂ O ₃ in excess.	HgCl ₂ as Hg. Found.	Error.
	Grm.	C.m.s.	°C.	Minutes.	C.m.s.	Grm.	Grm.
1.	0.0738	50	36	40	16.68	0.0494	0.0244 -
2.	0.0741	50	70	15	15.42	0.0738	0.0003 -
3.	0.0741	75	70	12	16.07	0.0733	0.0008 -
4.	0.0744	50	70	10	14.6	0.0755	0.0011 +
5.	0.0764	50	72	7	6.77	0.0771	0.0007 +
6.	0.0762	50	75	10	8.54	0.0799	0.0037 +
7.	0.0756	50	73	15	9.99	0.0815	0.0059 +
8.	0.0774	50	68	15	10.84	0.0767	0.0007 -
9.	0.0745	75	69	7	6.62	0.0805	0.0060 +
10.	0.0736	50	68	5	15.82	0.0714	0.0022 -

TABLE III.

	HgCl ₂ taken as Hg.	Volume at beginning.	Temp.	Na ₂ S ₂ O ₃ in excess.	HgCl ₂ found as Hg.	Error.
	Grm.	C.m.s.	°C.	C.m.s.	Grm.	Grm.
1.	0.0749	50	70	4.15	0.0751	0.0002 +
2.	0.0749	50	75	0.72	0.0728	0.0021 -
3.	0.0756	50	72	1.46	0.0759	0.0003 +
4.	0.0753	50	70	2.57	0.0750	0.0003 -
5.	0.0390	50	70	3.43	0.0395	0.0005 +
6.	0.0388	50	72	8.19	0.0390	0.0002 +
7.	0.0380	50	76	2.03	0.0393	0.0013 +
8.	0.1494	50	78	4.99	0.1498	0.0004 +
9.	0.1489	150	78	4.38	0.1512	0.0023 +
10.	0.1480	50	70	0.52	0.1438	0.0042 -
11.	0.1498	50	78	1.47	0.1540	0.0042 +
12.	0.1484	50	71	2.09	0.1517	0.0033 +
13.	0.1480	75	72	1.59	0.1509	0.0029 +

TABLE IV.

	HgCl ₂ taken as Hg.	Volume at beginning.	Temp.	Na ₂ S ₂ O ₃ in excess.	HgCl ₂ found as Hg.	Error.
	Grm.	C.m.s.	°C.	C.m.s.	Grm.	Grm.
1.	0.0759	100	60	3.06	0.0766	0.0007 +
2.	0.0384	100	60	2.81	0.0387	0.0003 +
3.	0.1498	100	60	1.1	0.1500	0.0008 +
4.	0.1503	100	60	1.63	0.1506	0.0003 +
5.	0.1479	100	60	2.41	0.1480	0.0001 +
6.	0.1489	100	60	2.12	0.1503	0.0014 +
7.	0.2244	100	60	2.63	0.2259	0.0015 +
8.	0.1490	100	60	2.33	0.1484	0.0006 -
9.	0.0758	100	60	2	0.0762	0.0004 +
10.	0.0383	100	60	2.58	0.0379	0.0004 -

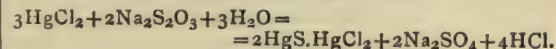
(c) *Mercuric Chloride*.—With mercuric chloride the end of the process is not so easily seen. The very dilute solution is acidified with hydrochloric acid, heated nearly to boiling, and the thiosulphate cautiously added so long as a white precipitate is seen to form; any great excess of the precipitant produces a dirty-looking colour. Filtration is necessary to distinguish the exact ending of the reaction. One c.m.³ of 1/20 normal thiosulphate = 0.015 Hg or 0.0162 HgO.

Fresenius ("Quantitative Analysis") gives practically the same directions, but omits all mention of that portion of the process dealing with mercurous nitrate.

In view, therefore, of the scant information available on the subject, and of the apparent difficulty of working the process accurately according to the directions given, an attempt was made to ascertain whether the careful regulation of temperature, dilution, and amount of acid present, might not produce beneficial results.

That portion of the process dealing with mercuric chloride was first taken up. The mercuric chloride used was pulverised, dried at 100°, and its purity proved by several determinations as mercuric sulphide. The sodium thiosulphate was made up of approximately 1/20-n normal strength and standardised on decinormal iodine, which in turn was titrated against decinormal arsenious acid made from pure re-sublimed arsenious oxide.

For the action of sodium thiosulphate upon the mercuric chloride Scherer gives the equation—



According to my experience, the action results in the formation of a dense white precipitate which refuses to settle either by shaking or standing, thus making it impossible to fix the end reaction by reading the first drop of thiosulphate which produces no further white precipitate in the solution containing the mercuric chloride. Recourse must be had, therefore, to filtering. By far the quickest and neatest method is to use the asbestos filter deposited on a large perforated platinum cone (*Amer. Chem. Journ.*, i., 321). This cone is set in a glass funnel by means of a rubber connector, and the funnel is passed through the stopper of a large side-necked Erlenmeyer connected with an exhaust-pump. A little asbestos fibre shaken in the liquid to be filtered was found to be very beneficial in preventing the precipitate from running through the filter. In all the following experiments the thiosulphate was run into the solution containing the mercuric chloride in excess, the whole shaken up with asbestos fibre, filtered, and the excess of thiosulphate determined by 1/20th normal iodine. This method of procedure seems to be far preferable to attempting to catch the end of the reaction by running in the thiosulphate until the last drop produces no precipitate. In the experiments shown in Table I. no attention was paid to the temperature of the solution, and the thiosulphate was run in until the liquid turned brown. In every case the solution was allowed to stand until there was no further visible change of colour.

A glance at the table shows that the results are most irregular. In Table II. is seen the result of regulating the temperature, and the length of standing after the addition of the sodium thiosulphate.

These results, although better than those of Table I., are still very uncertain. On the supposition that the change from white to black, which takes place in the solution after the addition of an excess of sodium thiosulphate more or less quickly, according to the temperature, was due to an increased amount of HgS in the compound 2HgS.HgCl₂, the next step was to ascertain whether this could be avoided by stopping the addition of the thiosulphate at the first indication of a change of colour in the white precipitate, diluting the solution with a large amount of cold water, and immediately throwing it on the filter. The accompanying Table (III.) shows the result of the experiments.

the thiosulphate cautiously added from the burette, vigorously shaken meanwhile, until the last drop produces no further precipitate. Scherer recommends that when the greater part of the metal is precipitated the mixture should be diluted to a definite volume, the precipitate allowed to settle, and a measured quantity of the clear liquid taken for titration; the analysis may then be checked by a second titration of the clear liquid if needful. One c.m.³ of 1/20 normal thiosulphate = 0.05 of Hg or 0.0162 of HgO.

In the case of quantities of mercuric chloride up to 0.1 grm. the results shown in Table III are very satisfactory, but when larger amounts of mercuric chloride are used the errors again become prominent. In Table IV. the effect of lowering the temperature to 60° C. and of increasing the dilution to 100 c.m.³ is shown.

From this table it is plain that Scherer's process for the estimation of mercury in the form of mercuric chloride is capable of yielding accurate results if carried out under certain fixed conditions. These conditions, which must be closely adhered to, are as follows;—The solution containing the mercury in the form of mercuric chloride is placed in a litre flask, diluted to 100 c.m.³, and heated to a temperature of 60° C. The sodium thiosulphate in 1/20th normal solution is run in from a burette until the white precipitate formed begins to take on a brownish tinge. The solution is then diluted with cold water, some asbestos fibre added to coagulate the precipitate, and the whole is quickly thrown on the filter. After careful washing of the precipitate, the filtrate is diluted to a definite volume, 3 grms. of potassium iodide added, and the excess thiosulphate titrated with iodine and starch solution. The duration of the process need not exceed fifteen minutes. It is worthy of note that there is no necessity of using any hydrochloric acid in addition to that formed in the reaction. This certainly eliminates one probable source of error—the interaction of hydrochloric acid and sodium thiosulphate.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION.

General Monthly Meeting, November 5th, 1900.

Sir JAMES CRICHTON-BROWNE, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

Mr. W. H. Maw, Mrs. R. Middleton, and Dr. W. H. Perkin, F.R.S., were elected Members.

The special thanks of the Members were returned to Dr. Frank McClean, F.R.S., for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures, and to Dr. Rudolph Messel for his present of a Bronze Bust of Sir Humphry Davy.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

October 30th, 1900.

Prof. HORACE LAMB, F.R.S., President, in the Chair.

A PAPER on "*The Solubility of certain Lead-Glasses or Fritts used in the Preparation of Pottery Glazes*," by WILLIAM JACKSON and EDMOND M. RICH, was read.

The paper described experiments carried out to determine what factors, apart from chemical composition, affect the amount of lead oxide yielded to dilute hydrochloric acid by lead fritts as used by potters. It was found that the solubility is increased in a very marked manner by increase of fineness, so that it appears that if details are given of the solubility of fritts they should be accompanied by particulars of its degree of fineness. The solubility of the same fritt reduced to different degrees of fineness varied from 1 to 15 per cent of the material used. It was found also that after the action of the acid has proceeded for a short time it appears that the whole of the soluble lead has been extracted. This, however, was due, not to the absolute insolubility of the remainder, but to the formation of an insoluble layer on the surfaces exposed to the action of acid which protects the particles from further

action. By removing this layer by chemical or physical means it was found possible to extract more lead oxide from the fritt, and, by continually removing this insoluble layer, it was possible to extract continually more lead oxide, until practically the whole of the lead oxide passed into solution.

A discussion followed the reading of the paper, in which the President, Mr. Wm. Burton, F.C.S., and Mr. T. Turner (Organising Secretary to the Technical Instruction Committee of the Staffordshire County Council) participated.

NOTICES OF BOOKS.

A Treatise on Qualitative Chemical Analysis. ("Traité de Chimie Analytique Qualitative"). By LOUIS DUPARC, EMILE DEGRANGE, and ALFRED MONNIER. Geneva: Henry Kundig. Paris: Félix Alkan. 1900. Pp. 223.

FOR the proper recognition of the chemical characteristics of any particular element, it is necessary to be thoroughly acquainted with its properties. With this object in view the authors have given *in extenso* all the reactions of the bases and acids, and have united the bases in four groups, established not so much on chemical analogies as on the wide methods of separation utilised in analysis. It would be useless to attempt chemical analysis without previously having acquired a general knowledge of inorganic chemistry, and especially of the atomic theory, the nomenclature of compounds, and of the mechanism of reactions and chemical equations. Without this preliminary knowledge practical work is apt to degenerate into purely mechanical operations, the student getting into the habit of adding so many drops from bottle No. 1, and so many from bottle No. 2, merely because the book tells him to, while he does not very often really understand what he is doing.

After devoting more than two-thirds of the book to what may be called preliminary work, such as a general examination of the materials and reactions utilised in analysis both by the wet and dry ways, detailed reactions of the bases and acids, the authors give a number of systematic tables for mineral analysis. These tables differ slightly from those ordinarily in use, inasmuch as groups 1 and 2 are combined so that there are only four groups in all. We can hardly see the necessity for this change, as the Hg, Ag, and Pb are, after all, separated from the rest of the usual second group, and then separated from each other in the usual manner.

The book closes with a graphic table of solubilities, a comprehensive table of contents, but no index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 16, October 15, 1900.

Preparation and Properties of the Carbides of Neodymium and Praseodymium.—Henri Moissan.—The oxides of neodymium and praseodymium, when heated in presence of carbon in the electric furnace, are transformed into the crystalline carbides of formulae NeC_2 and PrC_2 . These carbides decompose water in the cold, with production of a mixture of hydrogen carbides and the hydrated oxide. The author has already shown that the three carbides of the alkaline earths, prepared in the electric furnace, give, by their decomposition of water, only pure acetylene; on the other hand, aluminium carbide gives,

under the same conditions, only methane. It is known that neodymium and praseodymium belong to the cerium group, a group of metals placed, from consideration of its properties, between the metals of the alkaline earths and aluminium. It is curious to notice that neodymium and praseodymium carbide give, when placed in contact with water, a complex mixture of hydrocarbons, rich, however, in acetylene and methane. Further, it should be mentioned that the quantity of acetylene given by these different carbides diminishes from cerium to neodymium, and that neodymium and praseodymium, metals so closely allied as to have been for a long time confounded under the name of didymium, give with water a mixture of carbides of a very similar composition. Finally, the carbides of cerium, lanthanum, neodymium, and praseodymium correspond to the general formula RC_2 .

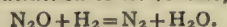
The Accessory Reactions of Electrolysis.—A. Brochet.—When a concentrated solution of sodium hypochlorite undergoes electrolysis and an estimation of the quantity of the salt left in solution is made, it is noticed that this quantity does not correspond to the theoretical number, more hypochlorite being decomposed than should be according to theory. The reverse is true in the case of the chlorate. At first sight this appears to be a case of non-accordance with Faraday's law, but experiment shows it to be the result of an independent reaction of the electric current. The author designates such a reaction as an accessory reaction of electrolysis. He investigates such reaction and finds that during the electrolysis of a solution of chloride the limiting value of the quantity of hypochlorite, due to oxidation and reduction, is 12.7 grms. of active chlorine per litre. He shows that if the reduction is suppressed this limiting value becomes 23.5 grms. The question then arises as to whether this limit is due only to the oxidation of the hypochlorite and if the accessory reaction is not the true cause. This question cannot be satisfactorily answered, owing to the difficulty of following the accessory reaction in the case of dilute solutions of hypochlorite. In all cases it is certain that, if the limit is due solely to the oxidation of the hypochlorite, it is useless to seek to suppress this oxidation, because a further check would be found due to limit of the accessory reaction.

Isopyrottritic Acid, a New Pyro-product of Tartaric Acid.—L. J. Simon.—In a former paper the author mentions an accessory product formed during the calcination of tartaric acid, which is an acid isomeric with pyrottritic acid, $C_7H_5O_3$, but distinct from it. He gives it the provisional name of isopyrottritic acid. The present paper contains an account of the properties and various reactions of this acid. When dissolved in water or an organic solvent, it gives with ferric salts, especially with the chloride, a very intense violet colouration. This colouration is very stable, not being alterable by time or heat. It is decomposed by strong acids, but on dilution will reappear if the acid is not present in too large quantities. Although it seems to be premature to attribute to this acid a definite composition from the facts mentioned in this and the preceding paper, it presents a certain analogy to salicylic acid, and so may be considered as a dihydroxy-oxybenzoic acid, $C_6H_4H_2(OH)CO_2H$.

MISCELLANEOUS.

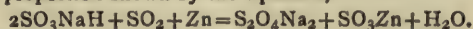
The Estimation of Nitric Acid in Gas Analysis.—G. von Knorre and K. Arndt.—It has been observed that when a mixture of nitric oxide and hydrogen in excess is passed through a capillary glass tube containing platinised asbestos, both nitrogen and ammonia are simultaneously collected, though in variable proportions, besides a certain amount of water vapour. The authors carried out their experiments at a much higher temperature in a platinum capillary tube heated to bright redness. Under these conditions, if the current is very slow, no ammonia is formed, and the reaction takes place according

to the following equation: $2NO + 2H_2 = N_2 + 2H_2O$, with the contraction of 1.5 times the volume of NO. In the same manner nitrous oxide reacts under similar conditions with an equal contraction of its volume,



By this means we are enabled to make analyses of the following mixtures:—NO with N_2O , NO with N, N_2O with N, N_2O with O, &c.—*Berichte*, xxxii., p. 2136.

Hydrosulphurous Acid.—A. Bernthsen and M. Bazlen.—One of the authors has previously (*Berichte*, vol. xiii., p. 2277) attributed the formula SO_2H or $S_2O_4H_2$ to Schutzenberger's hydrosulphurous acid instead of SO_2H_2 . The authors have now succeeded in preparing the neutral hydrosulphite of sodium in a state of purity. They treat powdered zinc with monosodic sulphite in the ordinary manner, and immediately add sulphurous acid in the proportion shown by the equation,—



Milk of lime is then added in slight excess, and the solution filtered. This filtrate contains only hydrosulphite of sodium. In this manner commercial solutions of this salt can be prepared at 15–16° B., of which 5 kilos. will suffice to reduce 5 kilos. of indigo. If such solutions are treated with sea-salt the hydrosulphite is precipitated in the pure state, in the form of crystals; the same will occur even if we add NaCl to the warm liquid and allow to cool. NaHO may also be used instead of NaCl. The analysis of the salt leads to the formula $S_2O_4Na_2 + 2H_2O$. It occurs in thin prisms with a vitreous lustre, 15 m.m. in length, easily oxidisable in moist air, but lasting for days without change in dry air, and fairly stable in dry air in a closed vessel. The dried salt burns at a dull red heat with a blue flame, and gives off SO_2 . This preparation was the subject of a German patent of the 23rd May, 1899, by the Badische Anilin und Soda-Fabrik. M. A. Nabl has recently (*Mon. f. Chim.*, 1899, p. 679) prepared hydrosulphite of zinc, S_2O_4Zn , in the solid state by the action of SO_2 on granulated zinc in absolute alcohol. M. Grossmann admits the existence of acid salts; they, like the free acid, should not be very stable, for the addition of a strong acid to the solution of the pure sodium salt gives a red colouration, quickly followed by a deposit of sulphur.—*Berichte*, vol. xxxiii., p. 126.

Distillation in Vacuo, and on some Regular Laws Obeyed by Liquids and Vapours in Vacuo.—F. Krafft.—When we boil, in vacuo, a substance having a high molecular weight, the operation proceeds in a very similar manner to distillation at the ordinary pressure, in this sense, that we observe a more or less thick layer of vapour above the surface of the liquid, according to whether we heat strongly or not, and quite distinct from the vacuum above, so that 2 or 3 c.c. above the limit cathodic rays may be made to pass. When this layer of vapour is very thin the temperature of the vapour is, to a fraction of a degree, the same as that of the boiling liquid, but if the layer is thick it exerts pressure on the liquid and retards its boiling, so that the upper layers of the vapour are several degrees cooler than the lower layers or than the liquid itself; other conditions being equal, however, the differences are proportional to the thickness of the column of vapour. The author has verified this with the fatty acids and with the saturated carbides. In the same series of homologues, the differences of temperature between the boiling liquid and the lower layers of vapour, at equal thicknesses of the latter, is proportional to the molecular weight. The author next deals with the difference between the fusing-points of substances (the fatty acids, the saturated carbides, the olefines), and their boiling points in vacuo. For the same series of homologues it increases from one term to another in arithmetic progression, or, in other words, proportionally to the molecular weight. For the normal paraffins the rate of progression is 4.22°, for the saturated fatty acids 4.9°.—*Berichte*, vol. xxxii., p. 1623.

Conditions of Crystallisation of Colloidal Saline Solutions.—F. Krafft.—Alkaline soaps dissolved in warm water are deposited, on cooling, in a gelatinous form, and this deposit takes place at a temperature slightly lower than that of the fusing-point of the free acid. For the homologues of a high order, like palmitic or stearic acids, the difference is only a fraction of a degree. The author finds that the salt is entirely hydrolysed in aqueous solution, and that the fatty acid, although insoluble, is held in suspension in the state of a colloidal emulsion. This solution can only exist above the fusing-point of the acid. In the case of the lower homologues, the solubility of these latter lowers the point of solidification. Another cause of this lowering exists in the affinity of the alkali for water; the potash soaps remain gelatinous at lower temperatures than the soda soaps. The author has also examined the solidification of aqueous solutions of salts formed of a strong acid united with a weak organic base. Here the results are less striking; the lowering of the point of deposition of the salt below the fusing-point of the free base is much more considerable than in the preceding case. However, it is only 1—3° for hydrochlorate of hexadecylamine. M. Krafft proposes the name of *globomorphous* in stead of amorphous, to indicate the state of the colloidal solutions solidified without crystallisation, admitting that the molecules in such solutions are animated by movements of rotation on themselves, and that they often deposit globular aggregations on cooling.—*Berichte*, xxvii., p. 1596.

MEETINGS FOR THE WEEK.

THURSDAY, 15th.—Chemical, 8. "The Bases contained in Scottish Shale Oil," by F. C. Garrett, M.Sc., and Jas. Smythe, B.Sc., Ph.D.

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Glasgow, October 31st, 1900.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2138.

THE MUTUAL RELATIONS OF IRON, PHOSPHORUS, AND CARBON, WHEN TOGETHER IN CAST-IRON AND STEEL.*

By J. E. STEAD, F.I.C., F.C.S.

(Concluded from p. 223).

ON THE INFLUENCE OF CARBON WHEN MELTED WITH IRON CONTAINING PHOSPHORUS.

WHEN saturated solid solutions of phosphide and iron are melted with increasing quantities of carbon, the effect is very pronounced at first, but comparatively slow after 1 per cent of phosphorus as phosphide has been thrown out of solution. This is shown by the following table:—

Nos.	Carbon. Per cent.	Phosphorus.		
		In free Fe_3P .	In solution.	Total.
		Per cent.	Per cent.	Per cent.
1.	nil	nil	1.75	1.75
2.	0.125	0.18	1.37	1.55
3.	0.180	0.59	1.18	1.77
4.	0.70	1.00	0.75	1.75
5.	0.80	1.06	0.70	1.76
6.	1.40	1.16	0.60	1.76
7.	2.00	1.18	0.55	1.73
8.	3.50	1.40	0.31	1.71

That the first portion of phosphorus should be easily removed is not surprising, for, as has been shown, on very slowly cooling a portion of the same iron free from carbon, nearly half of the phosphorus separated without any internal pressure from a third element. When 1 per cent of carbon is present, only 0.70 per cent of phosphorus remains in solid solution and 1.05 separates. With 3.5 per cent carbon this is reduced to 0.31 per cent.

An interesting instance of the effect of carbon in throwing out phosphide was found in a "bear," consisting of partially dephosphorised metal which had remained in the bed of a basic-lined open hearth steel furnace, when it was cooled down for re-lining. The analysis of this metal was as follows:—

Carbon	1.230 per cent
Manganese	0.45 "
Silicon	0.06 "
Sulphur	0.018 "
Phosphorus	1.38 "
Phosphorus in solid solution ..	0.62 "
Phosphorus in free phosphide ..	0.76 "

The microscope revealed the presence of large crystalline grains of pearlite, in which were embedded perfectly formed idiomorphic crystals of phosphide of iron, globules of phosphide eutectic, and irregularly-shaped masses of carbide of iron. The grains were surrounded by compound envelopes of carbide and phosphide of iron, the phosphide of iron being enclosed in the carbide.

Mr. E. H. Saniter, who primarily examined this specimen, found that, by crushing to fine powder and sieving off the finest part of the crushings, he was enabled to get the pearlite grains in a separate state. These he found, on analysis, to contain 0.62 per cent of phosphorus, a figure corresponding identically with that yielded by the chemical method in the laboratory of the writer; a figure which also corresponds very closely with the results given in Nos. 5 and 6 in Table II. These figures lead us to the conclusion that martensite, in presence of an excess of

phosphide of iron, will dissolve and retain in solid solution between 0.6 and 0.7 per cent phosphorus as phosphide of iron.

The continuity of the phosphide areas in the sample was very remarkable. On heating a portion of the metal in contact with the absorbent material oxide of iron, at a temperature of between 900° and 1000° C., a large portion of the eutectic simply ran out of the mass, and was absorbed in the surrounding oxide of iron. The analyses of the metal before and after treatment are as follows:—

	Before.	After.
	Per cent.	Per cent.
Phosphorus	1.38	0.91
Carbon	1.23	traces
P in Fe_3P (free)	0.76	0.18
Do. (solution)	0.62	0.73
Phosphorus lost — about ..	—	0.47

The phosphide of iron had evidently combined with a portion of the carbide of iron and the surrounding iron to form a fusible eutectic. This, soon after it became liquid, escaped or liquated from the mass, the grains falling together and uniting perfectly. The oxide of iron, on long-continued heating, eventually removed the carbon.

At one time during the heating each grain must have been practically floating in a fluid envelope.

In reflecting over these results it appeared probable that, if several pieces of sheet iron were placed one on the top of each other, and between each a little phosphide of iron eutectic in powder was placed, on heating to about 1000° C. they would all become welded together in the same way as the grains, and the excess of the phosphide would run out at the sides. A practical trial demonstrated that this actually took place. All the pieces were perfectly welded together, and, excepting at the points where the surfaces of the metals were not quite flat, no free phosphide remained.

On heating a sample containing a much larger quantity of phosphorus than 1.3 per cent, in the same way, but in which the phosphide areas were not continuous, no liquation occurred, excepting where the end of the eutectic areas terminated at the exterior of the piece.

When carbon is melted with iron containing less than the saturation quantity of phosphide, if the carbon is in sufficient quantity a part of the phosphide is thrown out of solution, even although the total amount of phosphorus is small.

The following table indicates the result of adding various quantities of phosphorus to steel containing about 1 per cent carbon:—

Nos.	Carbon. Per cent.	Phosphorus.	
		Per cent.	Phosphorus in free phosphide. Per cent.
1.	0.95	0.037	—
2.	0.96	0.099	0.002
3.	0.95	0.122	0.035
4.	0.96	0.347	0.065
5.	1.02	0.548	0.163

No free phosphide could be detected by the microscope in No. 1. In No. 2 it was doubtful if any was present. No. 3 contained traces. Nos. 4 and 5 contained distinct quantities. No. 5 ingot was very red-short, and broke to pieces with the first blow of the hammer.

The microscope showed that the phosphides did not form perfect and continuous envelopes around the grains, but occurred locally segregated at distances apart, and may be classed as typical with ordinary segregation which occurs more or less constantly with every ingot of steel which passes from the solid to the liquid state.

In all cases where segregation of phosphorus in steel has been studied, that element has been accompanied by carbon; in other words, they segregate together.

The segregates, as a rule, are located in those parts of the ingots or masses of steel which are last to solidify. The degree depends on three conditions, viz., the temperature, the mass, and the rate of cooling. With steel at a

* Read before the British Association (Section B), Bradford Meeting, 1900.

temperature much above its melting-point, and of great mass, when it is cooled very slowly, the segregation reaches a maximum.

Under the most favourable conditions there is generally some slight segregation.

It may be admitted that, in all cases when steel solidifies, there is a part which contains more carbon and phosphorus than the rest, and which is the last to solidify. This residuum, although not a eutectic, behaves very like one. It is a kind of mother-liquor. Its final position must depend on the way the greater mass of steel falls out of solution.

If the initial solidification commences at many centres the segregate must take the form of fluid, and finally solid cells, surrounding the parts which first solidified. So far as analysis could detect, in such a case there would be no segregation in the ordinary sense of the term, but it must exist nevertheless, distributed more or less evenly over the whole metal.

On the other hand, when the solidification commences at a few points and steadily progresses from those centres through comparatively great distances, a residuum, high in phosphorus and carbon, must be driven forward in front of the growing crystals till met by those growing in the other direction. When advance is no longer possible it finally solidifies, and forms the comparatively large segregates, easily detected by chemical analysis.

There can be no doubt that in all steels the part which first falls out of solution contains less carbon and phosphorus than that which finally solidifies. It might be urged that if that was so, the microscope would show at once the segregated carbon areas. It actually does so when it is very pronounced in the centre of large ingots, and in small ingots when the carbon is above 0.9 per cent, but not in small masses when the carbon is under 0.8 per cent, for the simple reason that after the residuum has solidified the carbon diffuses out of the areas and passes into the surrounding metal. The phosphides which diffuse very slowly must of necessity be left behind, and these can be sometimes detected by the microscope in high carbon steels, as has been shown. Phosphide of iron eutectic dissolves carbide of iron, but the carbide separates from it at its solidifying point. If then the solidifying phosphide and carbide are surrounded by a mass of iron capable of absorbing the liberated carbide, it is easy to understand how it happens that it is not found segregated with the phosphide.

The peculiar fringe of pearlite containing cementite plates radiating from the phosphide eutectic, in metals containing 1.75 per cent P, 0.12 per cent C, appears to confirm the conclusion that the carbide first segregated with the phosphide as a liquid, and that the carbon is thrown out at the point of solidification or afterwards in cooling down.

ON THE EFFECT OF INTRODUCING SOLID CARBON INTO SOLID PHOSPHORETIC IRON BY THE CEMENTATION PROCESS.

Samples containing variable quantities of phosphorus were carburised in a cementation furnace, at Sheffield, by Mr. T. W. Sorby. The results obtained were all of a very instructive character. It was found that, unless the amount of carbon introduced exceeds 1.20 per cent, no phosphorus is thrown out of solution, until the original phosphorus present exceeds 0.6 per cent, and if it is above that quantity the excess is thrown off as a liquid eutectic which liquates out of the mass, leaving the grains with from 0.6 per cent to 0.7 per cent phosphorus in solid solution.

A small sample, which originally contained 0.88 per cent phosphorus on carburising to 1.20 per cent carbon, contained when it left the carbon furnace only 0.63 per cent phosphorus, and only traces of free phosphide, the difference of 0.25 per cent having been expelled from solid solution by the carbon, and escaped entirely from the metal.

A larger piece of metal, containing about 1.96 per cent phosphorus, yielded a most remarkable result. It was of a very irregular shape, and about 6 c.m. in diameter at the thickest part. When it came out of the cementation furnace it was much scored on the outside, as if fluid metal had been run over it in thin streams. The lower part had adhering to it a solidified drop of metal, which had evidently liquated from the specimen. It was detached for analysis. On fracturing the metal a most instructive structure was revealed.

The metal before treatment was coarsely crystalline, with cleavage faces 3 c.m. across. After carburisation, excepting in a small kernel where the metal had escaped carburisation and where the original structure remained intact, the metal was entirely altered.

The external parts of the structure were coarsely granular, but between these and the kernel the crystalline masses were arranged in columns.

Portions were taken from fixed positions, and these were separately analysed with the following results:—

Description.	Carbon (per cent).		Phosphorus (per cent).		
	Carbon.	Total.	As free Fe ₃ P.	In solid solution.	Lost.
Kernel, centre ..	traces	1.96	0.94	1.02	none
Kernel, average.	0.23	1.94	0.94	1.00	none
1.	0.89	1.52	0.86	0.66	0.42
2.	0.93	1.30	0.61	0.69	0.64
3.	1.20	1.05	0.38	0.67	0.89
4. External layer	1.31	0.91	0.29	0.62	1.03

The drop of metal from the bottom of the piece contained:—

Phosphorus 4.86 per cent

The evidence is conclusive that, as the carbon passed into the metal, its dominating influence threw out the phosphide, equivalent to all excepting about 0.65 per cent.

MICROSTRUCTURE OF CEMENTED METAL.

A section of the metal revealed a most instructive structure when examined under the microscope. The central part, where there was no carbon, was traversed and cut up by plates or prisms of free phosphide of iron, and resembled the same metal after it left the malleable casting-furnace, a coincidence which removes the supposition that oxidising influences were responsible for the reorganisation of the phosphide from the condition it existed in in the metal before treatment. Near to the junction between the kernel and the columnar grains, the eutectic was bordered with a beautiful fringe of pearlite. The cementite laminae radiated from the junction towards the centre, the base of which rested upon a layer of the phospho-pearlite eutectic. The kernel was more or less spherical, and was surrounded by a shell of the same eutectic. This brittle envelope made it easy to break away the surrounding metal, leaving the kernel intact. The radiating columnar masses were encased by a layer of the phosphide eutectic, and the latter was surrounded by a tooth-like formation of cementite. The mass of the columns consisted of pearlite in which were embedded oval, elliptical, and globular masses of the eutectic, some of which were encased by cementite. The amount of the phosphide eutectic decreased with the distance from the centre. The columnar structure terminated at a distance of 1½ c.m. from the centre, and was replaced by ordinary polygonal grains, the joints of which contained very little phosphide, but sufficient carbide to completely envelope them. Imprisoned in the centre of these grains were globular masses of eutectic, and at wide distances apart irregular-shaped masses of the same substance were segregated at the junction of 3 grains.

If the specimen carburised had been perfectly globular, and the carburisation regular at all times during the process, there would have been a spherical fluid area between the centre and the outside, dividing a globe of solid metal

n the middle from a solid shell at the exterior, more or less cut up by fluid cells through which the liquid eutectic would have continually flowed, and which would have eventually left the mass of metal and fallen into the charcoal surrounding it. Although the specimen was not globular, the fluid envelopment must have been developed and continual liquidation of the eutectic been effected.

It is difficult to explain the changes in structure without the hypotheses that there exist allotropic conditions of iron.

In a paper by the writer on the crystalline structure of iron, it was for the first time proved that the thermoperturbation at Ar. 3, between 800° and 900° C., was coincident with the complete reorganisation of the crystalline structure. The coarse-grained, brittle, soft iron, on heating to just above Ar. 3, was changed to material with very fine grain and of exceedingly tough character.

Phosphorus has been proved by M. Osmond and others to prevent the thermal change at Ar. 3, and the writer has found that coarse-grained phosphoretic iron on heating through 900° C. is not reorganised in structure. In fact, a rectangular piece of iron, obtained by cleavage from a large crystalline grain of that material, on heating to between 900° and 1000° C., retained its original orientation with cleavages parallel to those of the metal previous to heating. Pure iron, then, consists of β -iron between Ar. 2 and Ar. 3 and of γ -iron above Ar. 3.

When above 1.25 per cent phosphorus is present in solid solution in iron, it is of β -iron between Ar. 2 and above 1000° C. γ -Iron cannot exist in presence of much phosphorus.

It is clear, then, that as carbon passed into the β -iron, expelling phosphorus from solid solution, the allotropic change under the influence of carbon must have been coincidentally effected, accompanied by a change or reorganisation of the crystalline structure.

A similar kind of columnar structure was developed on decarburising a bar of steel containing 0.21 per cent carbon at a temperature just under 800° C. It was at first difficult to account for the growth of the crystals in this peculiar way; but, on reflection, and knowing that carbon lowers the point at which the change from β to γ is effected, and knowing that γ -iron free from carbon cannot exist at a temperature under 800° C., it will be seen at once that the γ -iron existing under the influence of carbon at 800° must have changed its state when the carbon was removed, and as the removal of the carbon took place steadily from the outside towards the interior, the columnar crystals were formed coincidentally with the passage from γ to β condition—exactly the reverse of what must have taken place when the phosphorus was expelled by the introduction of carbon into the phosphoretic β -iron.

Although carbon in entering into iron containing phosphorus throws phosphide out of solid solution, it limits the amount of carbon which can be absorbed by the iron, and when 15.58 per cent phosphorus is present, the Fe_3P will not absorb carbon even by melting it with charcoal at a white heat. The result of repeated trials has shown that the carbon capable of being absorbed and retained by iron varies approximately inversely with the proportion of phosphide. Thus, if 50 per cent phosphide of iron and 50 per cent of free iron are melted together in contact with charcoal, the carbon absorbed will be only about half as much as if no phosphide was present. The following table shows practical results of melting iron and phosphorus with an excess of carbon:—

Analysis of mixture.		Carbon in melted metals. Per cent.	Fracture.
Iron. Per cent.	Phosphorus. Per cent.		
100	none	4.15	White.
96	4.10	3.25	"
93	7.90	2.00	"
87	13.00	0.70	"
83	16.00	nil	"

ON THE ACTION OF HYDRACIDS ON STEELS CONTAINING CARBON AND PHOSPHORUS.

Referring to the peculiar behaviour of hydracids upon solid solutions of phosphorus in iron, it will be remembered that as the phosphorus is more concentrated the less proportion of it is evolved as phosphine gas. The results of experiments made by M. Osmond have shown that the amount of carbon present influences the proportion of phosphorus evolved as phosphine, PH_3 ; and the experiments of the writer have fully confirmed his results. As the carbon is increased, less and less of the phosphorus present is gasified on dissolving the metal in acid. The only explanation of this peculiarity is based on the assumption that the carbon dominates the greater part of the iron and concentrates the phosphorus into the balance, and that, therefore, as the carbon is increased, the residuum of phosphorus and iron becomes a more and more concentrated solid solution of phosphide in the iron, and behaves in the same way when dissolved in acid as solid concentrated solutions which are free from carbon.

DIFFUSION OF SOLID PHOSPHIDE IN SOLID IRON.

It has been long known that carbon or carbide of iron will diffuse into iron, and Sir W. Roberts-Austen has shown that certain metals will diffuse into lead.

Prof. Arnold has proved that phosphide of iron will diffuse into iron at 1000° C. The results of the writer's observations, that solid phosphide falls out of solid solution and assumes the form of idiomorphic crystals, is strong evidence of molecular movement and diffusion of the dissolved substance in the solid solvent.

THE TITRATION OF MERCURY BY SODIUM THIOSULPHATE.*

By JOHN T. NORTON, Jun.

(Concluded from p. 230).

IN dealing with the estimation of mercury in the form of mercurous nitrate, the same method of procedure was employed as in the case of mercuric chloride. A solution of mercurous nitrate was prepared by dissolving as much as possible of 20 grms. of the salt in about 200 c.m.³ of water, filtering off the clear liquid and diluting to a definite volume. The standard of the solution was determined by precipitation as metallic mercury by means of the electric current. Contrary to the statement made in Sutton, the brown precipitate of Hg_2S , formed as shown in the equation,—



does not settle and leave a clear supernatant liquid, but the solution remains cloudy, and it is impossible to see any end reaction. Although the conditions of dilution, temperature, and amount of acid present were carefully considered, no arrangement or adjustment of these conditions was found under which satisfactory results could be obtained. Table V. gives the result of experiments.

The errors in experiments 1, 3, 4, 5, 6, 10, 11, 12, and 17 are, proportionally to the amount of material handled, practically the same, and this fact caused me to make a careful revision of all standards; but no mistake could be found. The reaction upon which the process depends requires the formation of Hg_2S , but this mercurous sulphide breaks down immediately into mercuric sulphide and mercury. The latter is probably acted upon by the free nitric acid present to form mercuric nitrate, which in turn is transformed into the compound $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$ by the action of the thiosulphate. At any rate, with an error so large, whatever its source may be, the process is plainly impracticable.

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1900, vol. x., No. 5.

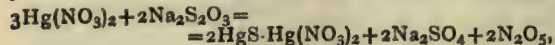
TABLE V.

Hg ₂ (NO ₃) ₂ taken as Hg.	HNO ₃ (1:3).	Volume at be- ginning.	Temp.	Na ₂ S ₂ O ₃ in excess.	Hg ₂ (NO ₃) ₂ found as Hg.	Error.
Grm.	C.m.s.	C.m.s.	°C.	C.m.s.	Grm.	Grm.
1. 0'0148	none	50	50	4'28	0'0129	0'0019-
2. 0'0148	none	75	60	4'45	0'0117	0'0031-
3. 0'2976	none	300	60	12'67	0'2760	0'0216-
4. 0'1488	none	100	40	2'19	0'1386	0'0102-
5. 0'1488	none	100	50	6'92	0'1378	0'0110-
6. 0'1488	none	200	50	0'78	0'1388	0'0100-
7. 0'0744	none	100	65	0'73	0'0636	0'0108-
8. 0'0744	1	100	55	0'49	0'0733	0'0011-
9. 0'0744	2	100	40	1'16	0'0660	0'0084-
10. 0'0744	1	100	55	1'35	0'0685	0'0059-
11. 0'0744	1	100	55	0'82	0'0686	0'0058-
12. 0'0744	1	200	55	1'71	0'0685	0'0059-
13. 0'0744	4	100	40	1'77	0'0649	0'0095-
14. 0'0744	5½	100	40	1'34	0'0645	0'0099-
15. 0'0744	1	100	45	1'71	0'0654	0'0090-
16. 0'0744	10	100	45	1'55	0'0669	0'0075-
17. 0'1488	1	100	40	0'73	0'1391	0'0097-

TABLE VI.

Hg(NO ₃) ₂ taken as Hg.	Volume at be- ginning.	HNO ₃ (1:3).	Temp.	Na ₂ S ₂ O ₃ in excess.	Hg(NO ₃) ₂ found as Hg.	Error.
Grm.	C.m.s.	C.m.s.	°C.	C.m.s.	Grm.	Grm.
1. 0'1167	200	none	60	0'46	0'1384	0'0217+
2. 0'1167	100	1	60	3'63	0'1348	0'0181+
3. 0'1167	100	2	60	0'23	0'1375	0'0208+
4. 0'1167	100	none	60	0'17	0'1360	0'0193+
5. 0'1167	300	none	21	0'12	0'1232	0'0065+
6. 0'1167	300	none	21	0'15	0'1375	0'0208+
7. 0'1167	200	none	21	11'8	0'1461	0'0294+
8. 0'1167	200	20	21	15'97	0'1403	0'0236+
9. 0'1278	200	none	21	5'23	0'1647	0'0369+
10. 0'1278	200	none	21	1'35	0'1653	0'0375+
11. 0'1278	100	none	21	1'43	0'1662	0'0384+
12. 0'0752	200	none	21	2'09	0'0996	0'0244+
13. 0'0255	100	none	21	2'01	0'0280	0'0025+
14. 0'0255	200	5	21	3'44	0'0264	0'0009+
15. 0'0255	200	10	21	0'85	0'0334	0'0079+
16. 0'0255	300	none	21	1'96	0'0264	0'0009+
17. 0'0255	200	none	21	1'9	0'0287	0'0032+
18. 0'0255	200	none	21	1'76	0'0290	0'0035+
19. 0'0639	200	none	60	1'53	0'0831	0'0192+

The third step in Scherer's process deals with the action of sodium thiosulphate on mercuric nitrate. In the following experiments a solution of mercuric nitrate was prepared either by dissolving as far as possible 20 grms. of mercuric nitrate in about 200 c.m.³ of cold water, filtering off the supernatant liquid, and diluting to a definite volume (Expts. 1-8), or by dissolving the salt in strong nitric acid and diluting (Expts. 9-19). The standard of the solution was obtained by precipitation as metallic mercury by means of the electric current. The yellow precipitate, formed according to Scherer's reaction,



on adding the sodium thiosulphate, settles much better than in the case of either mercuric chloride or mercurous nitrate; but, as the supernatant liquid takes on a permanent yellow colour towards the end of the reaction, it is impossible to see when the thiosulphate produces no further precipitation. On this account, therefore, the same method of procedure was adopted as in the case of the mercuric chloride and mercurous nitrate, *i.e.*, filtration and titration of the excess of sodium thiosulphate with iodine and starch solution. The result of the experiments is shown in Table VI.

These results seem to show the impossibility of obtaining accurate results according to Scherer's method for the

determination of mercuric nitrate by direct titration with sodium thiosulphate. The constant plus error cannot be accounted for on the hypothesis that the nitric acid present decomposes the sodium thiosulphate, for in that case the error would lie in the other direction. It is more probable that the constitution of the compound $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$ is not definite enough to make it the basis for an analytical process.

In conclusion I wish to thank Prof. F. A. Gooch for his kind advice and assistance.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 228).

Dilatometer Experiments.

Experiment 1.—Amorphous selenium in aniline. The following readings were obtained:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
20'1°	9	12:30	21°	10'7	9:25
—	9	12:45	70	125'2	10:40
29'9	32'5	1:15	—	123'8	10:45
—	32'5	2:45	—	120'5	10:52
40'2	56'7	3:20	—	118'5	10:56
—	56'7	3:50	65'5	104'8	11:15
49'8	79	4:20	—	104'3	11:35
—	79	4:50	—	104'2	11:56
60'1	103'2	5:10	59'9	90'8	12:15
—	103'2	5:35	—	90'8	12:40

The material was then slowly cooled to room temperature.

23'2	3'2	2:28	71	116'8	9:42
23'1	3'0	2:40	—	117'0	11:00
22'5	2'0	4:00	80'2	138'3	11:17
69'6	113'6	4:15	—	138'3	11:31
—	113'7	4:33	97	177'3	12:22
70'8	116'5	4:36	—	177'3	12:37
—	116'3	5:00	—	—	—

The first group of values shows that amorphous selenium in aniline shows no immediate change in volume when heated to 60°. (Later experiments have shown that there is a change when amorphous selenium remains in contact with aniline, even at ordinary temperatures; but this goes on comparatively slowly). The second group shows that at 70° a change sets in, which continues, though slowly, when the temperature is lowered to 65°; the apparent checking of the reaction at 60° was probably due to the fact that all the selenium was already transformed. It is important to notice that there was no sign of a tendency to return to the original volume when the temperature was maintained for twenty-five minutes at 60° and then slowly lowered to the temperature of the room. The remaining values show that no further change goes on up to 97°; the slight variations in tenths of a millimetre on the scale are not to be regarded as significant. In this experiment it was noticed that at 40° the selenium had shrunk together to about half of its original volume, and when the temperature had reached 50° it had become almost black and formed a small mass in the bottom of bulb.

Experiment 4.—Amorphous selenium in aniline, using a larger quantity of selenium than in Expt. 1. In this experiment, as in many which follow, the rise in temperature of the bath was slow and continuous, and readings were taken at intervals; not all of these are recorded here, but enough to make it possible to reconstruct the expansion curve; where any change was perceptible, the temperature was held constant for a time at that point. The selenium used in this experiment was first heated to 50°, to facilitate the liberation of air bubbles which adhere to the powder.

* From the *Journal of Physical Chemistry*, vol. iv, No. 6.

Temp.	Scale.	Time.	Temp.	Scale.	Time.
19°8'	10°3	12 : 20	—	90°3	3 : 03
60°1	97°0	12 : 40	Transferred to cold water.		
—	97°2	12 : 43	20°2	3	3 : 09
60	91	3 : 00	—	3	3 : 40

After standing over night :—

17	—2	9 : 35	66	89	12 : 05
28	18	9 : 50	—	64°5	12 : 50
35	35	10 : 02	—	61	3 : 00
43	52	10 : 15	69	67	3 : 05
48	63	11 : 22	79	87°5	3 : 23
60	87°5	11 : 48	90	109°5	3 : 45
66	95°5	11 : 58	100	129	4 : 15

The dilatometer was then cooled down, and in a subsequent experiment, lasting about four hours, the temperature was slowly raised from 72° to 202° without any irregularity in the expansion curve being observed.

In Experiment 4, the contradiction took place in two different stages, separated by a period of cooling and then a slow rise in which the temperature was maintained for one and one-half hours between 43° and 60° without any return toward the original readings. This confirms the evidence of Experiment 1, showing that when both forms of the substance are present, the change is still only capable of going one way, *i.e.*, is irreversible. In a later experiment this dilatometer was heated in direct sunlight during forty-five minutes from 113° to 162°; the readings give no indication of any change in the selenium. It may be as well to state here, what is later established, that the denser form obtained in all these dilatometric experiments is metallic selenium of density 4·8.

It was desirable after completing these experiments to heat the dilatometer up to 220° in order to transform the selenium again into the liquid modification, without being under the necessity of removing it from the bulb. It did not prove practicable to do so in aniline, on account of the evolution of gas, which begins in that liquid at temperatures varying from 160° upwards, according to the pressure within the tube. Aniline was therefore abandoned, and a few experiments were tried with glycerin; the same difficulty was encountered with this liquid, too; nevertheless, several sets of observations were made, up to about 200°, with the result that the transformation of vitreous selenium was found to begin at about 75°, no further change being observable up to 200°, nor was there any sign of a reverse transformation when the tube stood at 25°. The experiments of Siemens and others on the conductivity of selenium indicated the possibility of some change taking place in sunlight at 160° or above, but although the tube which contained metallic selenium was kept for half an hour under a burning-glass, in a bath whose temperature varied between 156° and 172°, no change was found to occur.

Some experiments were then made in quinoline. Starting with metallic selenium, the dilatometer was heated in the dark for five hours between 154° and 196° without any indication of a change at any point. Subsequent heating for three hours between 150° and 200° only confirmed this result. The tube was then brought into direct sunlight, placed under a burning-glass, and heated, on different days, for one and one-half hours between 150° and 180°, for one and one-half hours from 190° to 195°, and for one-half hour from 198° to 202°; the readings are, within the limits of experimental error, identical with the original observations when the heating was carried on in the dark. These observations make it extremely improbable that metallic selenium suffers any change either in the dark or in direct sunlight, when heated to temperatures between 150° and 200°. It does not of necessity follow that the element will behave in the same way when heated in a liquid capable of dissolving it, as it will when heated by itself; on the other hand, the probability is that any change which goes on in the substance taken by itself, which leads to the production of a more stable form, will take place only the more readily in presence of a solvent.

Thus, it will be shown later on that amorphous selenium, which is capable of existing by itself for an indefinite time without change, at ordinary temperatures, goes over rapidly, in the presence of pyridine and certain other liquids, to the metallic form.

The same difficulties which had been met with in working with aniline and glycerin were once more encountered with quinoline when the temperature was raised above 200°. It was supposed at first that all of these reactions were with the liquids themselves, but it seems more probable from later observations that the difficulty is due to small quantities of water which adhere to the selenium from the method of purification. The dilatometers when opened always had the odour of selenium hydride. Meanwhile it had been found that solid paraffin promised to give better results, and this material was then employed for several sets of observations. It was thus rendered possible to work freely between 20° and 230°, although the results of successive transformations into the metallic form did not always lead back exactly to the same reading, on account of the gradual accumulation in the selenium of gas bubbles, which, under the prevailing high pressures, did not free themselves from the mass. This difficulty was obviated later by opening the tube from time to time to let the bubbles escape.

Experiment 23.—Metallic selenium heated in paraffin from 60° to 210° shows no irregularity. When the temperature is raised to about 218°, the selenium begins to melt and expands; at 220° the melting was complete in half an hour, and on cooling, the vitreous form was produced. The readings are as follows :—

Temp.	Scale.	Time.
60°	30	11 : 55
172	257	12 : 10
200	315	
210	336	
218	360	12 : 15 (fusion begun)
222	412°5	12 : 49 (fusion complete)

the tube was then cooled rapidly—

57°5	57	12 : 55
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The dilatometer was then placed in a bath at 160°, whose temperature was rapidly rising. The level in the capillary rose at first, then rapidly fell, showing a sudden transformation from the vitreous to the metallic modification. The tube then stood in direct sunlight for an hour at about 200°. At the end of the time the reading was 311, almost identical with the above. Thereupon the temperature was raised to about 228°, and the material completely fused, after which the bath temperature was brought down to 200°, in order to determine what change takes place when melted selenium is maintained at that temperature. The readings are as follows :—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
225°	418	3 : 42	200°	351	4 : 24
199	367	3 : 45	—	344	4 : 33
199	363	—	—	339	4 : 40
198	359	3 : 47	—	335	4 : 48
198	357°5	3 : 49	—	330	4 : 55
198	357°5	3 : 52	—	325	5 : 03
197°5	356	4 : 01	—	322	5 : 15
199	356°5	4 : 10	—	320	5 : 25
199°5	355°5	4 : 15	—	320	5 : 36
200	353°5	4 : 20	—	319	5 : 46

The dilatometer was then cooled to 65°, where the scale reading was 30. This reading, like the final reading at 200°, is somewhat higher than that previously obtained. A few small bubbles of gas were observed in the bulb at the end of the experiment, and it is to them, no doubt, that the variations are to be attributed. This experiment in itself would not be conclusive without the confirmation of later observations; the values are given in detail to indicate the rate at which the change goes on at 200°.

The falling level in the first readings at 199° is not due to a change in the selenium, but to the lag of the instrument, which does not adjust itself at once to the changed bath temperature; a closer inspection shows that the transformation of the selenium did not set in until about half an hour later and was complete about an hour after it commenced. The rate is at first very slow, then increases and remains almost constant until near the end, when it is much retarded.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, July 5th, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

PROFESSOR OTTO PETTERSSON, of Stockholm, delivered the Nilson Memorial Lecture.

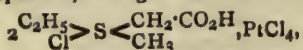
On the motion of Dr. ARMSTRONG, seconded by Prof. DEWAR, a vote of thanks was passed to Prof. Pettersson for his lecture.

The following are abstracts of the papers received during the vacation, and published in the *Transactions* :—

III. "Asymmetric Optically Active Sulphur Compounds; *d*-Methylethylthetine Platinichloride." By W. J. POPE and S. J. PEACHEY.

Although the earlier attempts of the authors to resolve methylethylthetine into optically active components were unsuccessful, they have since succeeded in preparing *d* methylethylthetine platinichloride. Methylethylthetine bromide was treated with silver *d*-camphorsulphonate. The residue, after evaporation at a low temperature, was dissolved in absolute alcohol and precipitated by the addition of anhydrous ether, and this treatment repeated about forty times, when a sparingly soluble fraction was obtained, which seems to be *d*-methylethylthetine *d*-camphorsulphonate. It melts at 118–120°, and gives $[\alpha]_D = +18.6^\circ$ and $[M]_D = +68.0^\circ$.

The *d*-bromocamphorsulphonate was similarly prepared. When either of these salts is dissolved in absolute alcohol, a little strong hydrochloric acid and an alcoholic solution of platinic chloride added, a yellow, crystalline platinichloride is deposited, having the constitution—



and giving $[\alpha]_D = +4.5^\circ$ and $[M]_D = +30.5^\circ$.

II2. "Sulvanite, a New Mineral." By G. A. GOYDER. This mineral was found in considerable quantity in some ore from a new mine near the Burra in South Australia. It appears to afford the first recorded instance of a sulphide mineral containing vanadium as one of its principal constituents.

The analyses given show that it consists of cuprous sulphovanadate, $3\text{Cu}_2\text{S} \cdot \text{V}_2\text{S}_5$. Its hardness is 3.5, and its specific gravity 4.0.

II3. "Estimation of Atmospheric Carbon Dioxide." By JAMES WALKER.

A modification of Pettenkofer's bottle method is described which gives results accurate to 0.1 vol. carbon dioxide in 10,000 vols. air, when a bottle of 2.6 litres capacity (Winchester quart) is employed. The usual error due to absorption of carbon dioxide during titration is avoided by filtering the residual baryta solution into a known quantity of hydrochloric acid, and titrating back with standard baryta. The filtration takes place under diminished pressure through asbestos contained in a Soxhlet filter tube, atmospheric air being entirely excluded during the process of filtering and washing. No special apparatus is employed, and an estimation occupies only half-an-hour.

II4. "On some Periodides of Substituted Oxonium Derivatives." By J. N. COLLIE, F.R.S., and B. D. STEELE, B.Sc.

During the investigation of the salts of tetramethylpyrone, it was noticed that when the solution of the iodide was allowed to evaporate in the air brownish crystals slowly separated, which were nearly insoluble in water. From their properties they seemed to resemble the periodides of the pyridine bases. It was found that when free iodine in potassium iodide solution was added to a solution of the hydriodide of tetramethylpyrone or of dimethylpyrone, an immediate crystalline precipitate was produced.

These periodides have the following constitution: from dimethylpyrone, $\text{C}_7\text{H}_5\text{O}_2\text{HI}_2$; from tetramethylpyrone, $\text{C}_9\text{H}_{12}\text{O}_2\text{HI}_2$. They lose iodine when heated, and are at once converted into di- and tetra-methylpyrone when treated with a solution of soda.

The action of iodine on the barium and sodium salts of dimethylpyrone proceeds in a quite different manner. The chief product is an oxidised iodine compound, $\text{C}_7\text{H}_7\text{IO}_3$, which possesses rather remarkable properties; it is not decomposed when warmed with solutions of soda or sodium ethylate, but gives free iodine at once when warmed with a mineral acid.

II5. "Condensation of Phenols with Esters of the Acetylene Series. II. Action of Phenols on Ethyl Phenylpropiolate and Ethyl Acetylenedicarboxylate." By SIEGFRIED RUHEMANN and FRED BEDDOW.

The authors describe ethyl-*s*-m-cresoxycinnamate and the products of its transformation as well as the reaction between phenols and ethyl acetylenedicarboxylate. They find that in the latter case aryl ethers of ethyl hydroxyfumarate are formed, and not the ethers of ethyl hydroxymaleate, which were expected; this has been proved by a comparison of the products with the compounds obtained by the action of the sodiophenolates on ethyl chlorofumarate. The aryl ethers of ethyl hydroxyfumarate, on hydrolysis with alcoholic potash, give the corresponding acids, which on heating are partially transformed into the aryl ethers of hydroxymaleic acid; these differ from their stereoisomerides in that lead acetate gives with their aqueous solutions precipitates of their lead salts, but not with the aryl ethers of hydroxyfumaric acid.

II6. "The Vapour Pressures, Specific Volumes, and Critical Constants of Di-isopropyl and Di-isobutyl." By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

The results here given, taken in conjunction with those of previous researches, show that an iso- or di-iso-paraffin bears very much the same relation to the isomeric normal paraffin as a lower does to a higher homologue. Thus the ratios of the absolute temperatures to the absolute critical temperatures, and of the volumes of saturated vapour to the critical volumes at corresponding pressures, as well as of the actual to the theoretical densities at the critical points, are higher for the normal paraffins, whilst the ratios of the volumes of liquid to the critical volumes at corresponding pressures are lower.

It was found that di-isopropyl shows marked peculiarities; it is exceptionally difficult to prepare by any method involving the combination of two $(\text{CH}_3)_2\text{CH} \cdot$ groups; the specific gravity at 0° and the critical pressure are higher than those of normal hexane, whereas these constants in all other known cases are lower for the iso- and di-iso-paraffin than for the normal isomerides; the critical density, the critical temperature, and the boiling-point are also exceptionally high.

II7. "The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Octane." By SYDNEY YOUNG, D.Sc., F.R.S.

The normal octane was obtained from Kahlbaum, and was easily purified by treatment with sulphuric and nitric acids and subsequent fractional distillation.

A comparison of the data for normal pentane, hexane,

heptane, and octane shows that the ratios of the absolute temperatures at any series of corresponding pressures to the absolute critical temperatures, and also the ratios of the actual to the theoretical densities at the critical points, increase slightly with rise of molecular weight, whilst the ratios of the volumes of liquid at corresponding pressures to the critical volumes diminish slightly.

The ratios of the volumes of saturated vapour to the critical volume are, on the whole, very slightly lower than for normal heptane, but are higher than for hexane or pentane.

118. "Separation of Neobornylamine from Bornylamine." By M. O. FORSTER and J. HART-SMITH, A.R.C.S.

In the course of attempts to separate neobornylamine from bornylamine, in addition to the hydrobromide, hydriodide, nitrate, sulphate, and benzoate of bornylamine, the following substances have been obtained.

Camphoroximeacetic acid, $C_{10}H_{16}NO \cdot CH_2 \cdot CO_2H$, which melts at $100-102^\circ$, and gives $[\alpha]_D = -5.9^\circ$; the sodium and bornylamine salts are well defined.

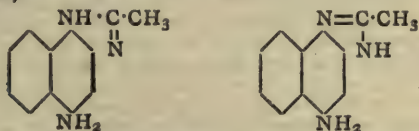
Bornylloxamide, $C_{10}H_{17}NH \cdot CO \cdot CO \cdot NH_2$, melting at 162° , which gives $[\alpha]_D = -24.1^\circ$.

Dibornylloxamide, $C_{10}H_{17}NH \cdot CO \cdot CO \cdot NH \cdot C_{10}H_{17}$, which melts somewhat indefinitely at 140° , and gives $[\alpha]_D = -29.6^\circ$.

Purified neobornylamine melts at 184° , and has $[\alpha]_D = -43.7^\circ$ in absolute alcohol. The benzylidene derivative is an oil which boils at 180° under 25 m.m. pressure.

119. "Aminoamidines of the Naphthalene Series." By RAPHAEL MELDOLA, F.R.S., and LEWIS EYNON, A.I.C.

It has been found by the authors that when dinitro-acetnaphthalide is reduced by iron and hydrochloric acid (Markfeldt, *Ber.*, 1898, xxxi., 1174), the ethenyltri amino-naphthalene produced is isomeric and not identical with that obtained when tin and hydrochloric acid are used (Meldola and Streatfield, *Trans.*, 1887, li., 691). In this paper it is shown that the isomerism is entirely attributable to the reducing agent, since the same dinitro-acetnaphthalide has been used throughout. Descriptions and analyses are given of Markfeldt's base and some of its salts, of the acetyl derivatives of both bases and their salts, and of the isomeric phenylazo-derivatives. The pronounced difference in the properties of the latter compounds first indicated the isomerism of the respective anhydro-bases. It is suggested that the isomerism may be explained by the structural differences indicated by the formulæ,—

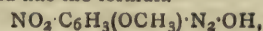


Experiments with the object of determining the constitution of the amino-amidines have been commenced, and the research will be extended in this direction. When the NH_2 group in Markfeldt's base is replaced by hydrogen by the diazo-method, an ethyldiaminonaphthalene is obtained which is apparently identical with that of Prager (*Ber.*, 1885, xviii., 2161).

120. "Note on the Elimination of a Nitro-Group during Diazotisation." By RAPHAEL MELDOLA, F.R.S., and ELKAN WECHSLER.

When acetorthoanisidine is nitrated with excess of fuming nitric acid in the cold in acetic acid solution, a dinitroacetanisidine is formed. This compound crystallises in light yellow needles, melting at $162-163^\circ$, and on hydrolysis by alcoholic sodium hydroxide gives a dinitro-anisidine, crystallising in bright orange needles, having a melting-point of $186-188^\circ$. This dinitroanisidine, on treatment with sodium nitrite and an acid, forms a diazo-compound which crystallises in ochreous scales or yellow

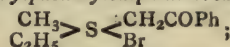
needles, having an exploding-point of about 178° . The diazo-compound has the formula—



so that one nitro-group is eliminated during the process of diazotisation. The corresponding iodoniromethyl-resorcinol crystallises in flat, yellow needles, melting at $115-116^\circ$. The nitroazo- β -naphthol derivative, obtained by combining the diazo-compound with β -naphthol in alkaline solution, forms glittering, bronzy-green scales decomposing at about 250° . The constitution of the new dinitroanisidine is being investigated, with the object of determining the particular configuration which is favourable to this easy displacement of a nitro-group.

121. "A Contribution to the Stereochemistry of Sulphur; an Optically Active Sulphine Base." By S. SMILES, B.Sc.

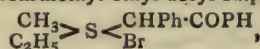
Methyl ethyl sulphide unites with ω -bromacetophenone to form methyl ethyl phenacylsulphine bromide,—



this, when treated in alcoholic solution with silver dextro- α -bromocamphorsulphonate, gives rise to two salts, the molecular rotation of the less soluble of which is $+250^\circ$, and of the more soluble $+289^\circ$. This points to the fact that the basic methyl ethyl phenacyl radicle possesses a molecular rotation in aqueous solution of over 20° .

From the less soluble salt a laevorotatory sulphine picrate was obtained as yellow needles (m. p. 125°) for which $[\alpha]_D = -9.3^\circ$ and $[M]_D = -39.3^\circ$. The dextro-rotatory picrate obtained from the more soluble salt (yellow needles, m. p. $123-124^\circ$) gave $[\alpha]_D = +8.1^\circ$ and $[M]_D = +34.2^\circ$.

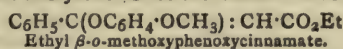
It was not found possible, however, to separate two stereoisomers from methyl-ethyl-desyl-sulphine bromide,—



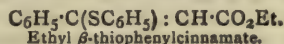
which was obtained as a colourless mass of deliquescent needles.

122. "Condensation of Phenols with Esters of the Acetylene Series. Synthesis of Benzo- γ -Pyrone." By S. RUHEMANN and H. E. STAPLETON.

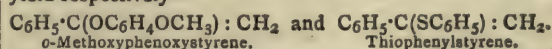
By the condensation of guaiacol and thiophenol with esters of the acetylene series the authors have obtained—



and—

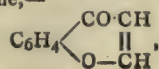


These esters, on hydrolysis with alcoholic potash, give the corresponding acids which lose carbon dioxide and yield respectively—



Ethyl acetylenedicarboxylate condenses with thiophenol to ethyl thiophenylfumarate, which is decomposed by alcoholic potash, forming phenyl disulphide ($C_6H_5S_2$). Along with the ethyl thiophenylfumarate, ethyl dithiophenylsuccinate is also formed, having probably the formula $CO_2Et \cdot C(SC_6H_5)_2 \cdot CH_2 \cdot CO_2Et$. The analogous oxygen compound, along with ethyl β -phenoxyfumarate, is obtained by the action of phenol on ethyl acetylenedicarboxylate.

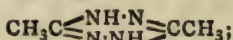
Ethyl β -phenoxyacrylate, by treatment with strong sulphuric acid, is not condensed into flavone, but decomposes into benzoylacetic acid along with oxalic and acetic acids. Ethyl phenoxyfumarate, however, partially undergoes the desired change, forming benzo- γ -pyrone-carboxylic acid, which, on heating, loses carbon dioxide, giving benzo- γ -pyrone,—



melting at 59° .

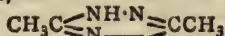
123. "Contributions to the Chemistry of Hydrotetrazines and Triazoles." By OSWALD SILBERRAD, Ph.D.

The action of hydrazine hydrate on diacetanilide gives dimethyldihydrotetrazine,—

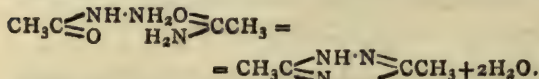


its hydrochloride melts at 232°. Benzoyl chloride decomposes it with the formation of *sym*-dibenzoyl-hydrazine and acetic acid.

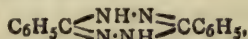
Nitrous acid converts it into dimethyltriazole nitrate (m. p. 125°), from which the hydrochloride (m. p. 199°) and the free base,—



(m. p. 142°, b. p. 258° at 752 m.m.), may be obtained. Its constitution is evident from its synthesis from acetamide and acetylhydrazine,—

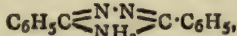


Diphenyldihydrotetrazine,—

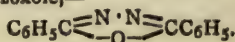


may be obtained in almost theoretical quantity by heating benzoylhydrazine with hydrazine hydrate to 230°. It melts at 264°; Pinner gives 258° (*Ber.*, 1894, xxvii., 1006).

Heated alone, benzoylhydrazine yields only traces of diphenyldihydrotetrazine, the chief products being diphenyltriazole,—



and diphenyldiazoxole,—



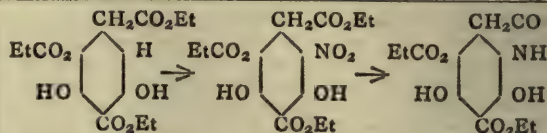
aa-Benzoylphenylhydrazone under similar treatment does not condense, but breaks down with production of benzophenone, benzoic acid, and benzoylanilide.

124. "Isomeric Dibenzylketone Benzalanilines and Deoxybenzoin Benzalanilines." By FRANCIS E. FRANCIS, Ph.D., B.Sc.

Three isomeric addition products of the two ketones, dibenzyl ketone and deoxybenzoin, with benzalaniline are described. For the sake of convenience these are termed α -, β -, γ -modifications. The α is obtained from the pure ketone, the β by the action of traces of piperidine on the α , or with greater difficulty on the γ , the γ by the action of traces of sodium ethylate on either the α or β . By the action of heat, the β and γ are transformed into the α -modification. The dibenzyl ketone benzalanilines are more basic than the deoxybenzoin benzalanilines; the former yield normal, whilst the latter give basic hydrochlorides. These salts are different in the case of α and β , but identical in β and γ . They are dissociated by water, giving the corresponding base, but with alcohol the α -hydrochloride appears to give a mixture of α and γ base, whereas the β or γ gives the α -modification nearly pure.

125. "Condensation of Methyl Acetonediacarboxylate. Constitution of Orcinoltricarboxylic Esters." By F. W. Dootson, M.A.

It is shown that a moderate temperature is sufficient to condense methyl acetonediacarboxylate to trimethyl orcinoltricarboxylate, and that a good yield of the latter is obtained. The constitution assigned to ethyl orcinoltricarboxylate by Jerdan is confirmed, and the similarity of the methyl and ethyl esters is shown by nitration and subsequent reduction, when a lactam structure results in both cases, proving that in orcinoltricarboxylic esters the remaining hydrogen atom of the benzene nucleus is in the ortho-position to the side chain, thus:—

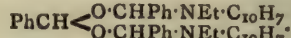
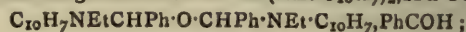


126. "Contribution to the Chemistry of the Aromatic Meta-diamines." By G. F. MORGAN, D.Sc.

In this paper the following compounds are described:—1-Bromo-2:4-phenylenediamine melting at 111–112°; its dibenzoyl and its diacetyl derivatives melting at 178.5° and 198° respectively; dibenzoyl 1-chloro-2:4-phenylenediamine, m. p. 178°, and chlorochrysoidine, $\text{PhN}_2\text{C}_6\text{H}_4\text{Cl}(\text{NH}_2)_2$, m. p. 149°; *m*-phenylenediacetyldichloramine, $\text{C}_6\text{H}_4(\text{NClAc})_2$, m. p. 150–151°; diacetyl 1:5-dichloro-2:4-phenylenediamine, m. p. above 260°; 1:5-dichloro-2:4-phenylenediamine melting at 136–137° and its dibenzoyl derivative at 187°.

Diacetyl-*m*-tolulylenediamine, when chlorinated and then hydrolysed, gives 5-chloro-2:4-tolulylenediamine, m. p. 120–121°; its diacetyl derivative melts at 239–240°.

127. "Action of Aromatic Aldehydes on Derivatives of β -Naphthylamine." By GILBERT THOMAS MORGAN, D.Sc. The compound, $\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2$, produced by the condensation of ethyl β -naphthylamine (2 mols.) with benzaldehyde (3 mols.) crystallises in colourless leaflets and melts at 148°. Its constitution may be represented by one of the following formulæ:— $\text{Ph}\cdot\text{CH}(\text{NEt}\cdot\text{C}_{10}\text{H}_7)_2$, $\text{Ph}\cdot\text{COH}$;



Its general behaviour is in accordance with the third of these; but freezing-point determinations seem to indicate that the substance, dissolved in benzene, corresponds with the second formula.

The following anhydro-bases and their hydrocyanides, derived from 1-chloro-2-naphthylamine and its bromine analogue, are also described in the paper:—Benzylidene-1-bromo-2-naphthylamine, m. p. 93–94°, and its hydrocyanide, m. p. 92°; the cumylylidene derivative and its hydrocyanide, melting at 100–101° and 120° respectively; the *p*-hydroxybenzylidene, and *o*-hydroxybenzylidene derivatives, melting respectively at 189–190° and 144°, and the corresponding hydrocyanides at 144° and 152°; *p*-methoxybenzylidene-1-bromo-2-naphthylamine and its hydrocyanide, melting at 107° and 140–143°; cinnamylidene-1-bromo-2-naphthylamine, m. p. 126°, and its hydrocyanide, m. p. 142–143°; benzylidene-1-chloro-2-naphthylamine and the corresponding cumylylidene derivative, melting respectively at 99° and 85°, and their hydrocyanides at 77° and 117°; cinnamylidene-1-chloro-2-naphthylamine, m. p. 134°, and its hydrocyanide, m. p. 155–156°; *p*-hydroxybenzylidene-1-chloro-2-naphthylamine and the corresponding *ortho*-isomeride, melting respectively at 191° and 153°, and their hydrocyanides at 152° and 148°; *p*-methoxybenzylidene-1-chloro-2-naphthylamine, m. p. 117°, and its hydrocyanide, m. p. 132°.

The following anhydro-bases do not combine with hydrogen cyanide:—*o*-Nitrobenzylidene-1-chloro-2-naphthylamine, m. p. 142°, and the corresponding bromo-compound, melting at 138°; *p*-nitrobenzylidene-1-chloro-2-naphthylamine, m. p. 151°, and its bromine analogue, melting at 154–155°.

128. "Action of Hydrogen Peroxide on Carbohydrates in the presence of Ferrous Salts. II." By R. S. MORRELL, M.A., Ph.D., and J. M. CROFTS, M.A., B.Sc.

Rhamnose when oxidised by hydrogen peroxide in the presence of ferrous sulphate yields an osazone which reacts with phenylhydrazine at the ordinary temperature to give rhamnosazone.

Similarly, cane sugar, when the hydrogen peroxide is neutral, is first "inverted" and then oxidised, since, on testing with phenylhydrazine, glucosazone is precipitated.

The action of potassium persulphate on glucose in the

presence of ferrous sulphate is slow at ordinary temperatures. On warming to 40°, oxidation proceeds more rapidly with formation of glucosone. The yield of the glucosone (measured by the weight of the glucosazone precipitate) is smaller than when hydrogen peroxide is employed as the oxidising agent.

129. "The Specific Gravities of the Halogens at their Boiling-points, and of Oxygen and Nitrogen." By J. DRUGMAN, Ph.D., and W. RAMSAY, F.R.S.

The determinations made by the authors of the specific gravities of the halogens at their respective boiling-points under atmospheric pressure have given the following results:—

Iodine boiling at 184.5°	has the sp. gr.	3.706
Chlorine " -33.6°	" "	1.507
Fluorine " -187°	" "	1.108

The specific gravity of fluorine was arrived at by using the data of Moissan and Dewar (*Proc.*, 1897, xiii., 180) and calculating the specific gravity at its boiling-point, corrections being made for the expansion of the liquid fluorine and the change in the specific gravity of amber. Amber was found to have the specific gravity 1.065 at 15° and 1.10 at -187°. The specific gravities of oxygen and nitrogen were found to be 1.1315 and 0.7914 at their respective boiling-points.

130. "On Hydroferrocyanic Acid." By K. C. BROWNING, B.A.

The purification and some of the properties of hydroferrocyanic acid are described. This acid begins to evolve hydrocyanic acid at 120°, and its decomposition is complete at 300°, ferrous cyanide being left as a pale yellow powder. Ferrous cyanide decomposes above 430° into iron, carbon, and iron carbide. Reasons are given for considering it to be an isocyanide, but when strongly heated it seems to decompose partly as if it were a normal cyanide.

From the decomposition of ethyl ferrocyanide it would seem that all the cyanogen groups present have the isocyanide arrangement.

131. "On the Nature of Metal-ammonia Compounds in Aqueous Solutions." Part I. By H. M. DAWSON and J. MCCRAE.

The nature of various ammoniacal salt solutions has been studied by determining the amount of ammonia extracted by shaking a known volume of the aqueous solution with a known volume of chloroform. If pure aqueous ammonia be shaken with chloroform at a constant temperature till equilibrium is established, this condition is characterised by the relationship $c_1/c_2 = \text{constant}$ (26.3), where c_1 = concentration of ammonia in water and c_2 that in chloroform.

When this is done with ammoniacal solutions of cupric sulphate, cupric chloride, zinc sulphate, cadmium iodide, and nickel sulphate, the constant is found to give much higher values, and hence the amount in combination with the salt may readily be deduced. Experiments with calcium chloride solution also indicate the formation of a complex metal-ammonia compound, but the amount of ammonia combined per molecule of salt is very much smaller than in the case of the other salts investigated.

Experiments were also made with ammoniacal copper oxide solution which indicate that the base $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$ is probably formed; the copper sulphate compound has the formula $\text{Cu}(\text{NH}_3)_4\text{SO}_4$.

PHYSICAL SOCIETY.

Ordinary Meeting, November 9th, 1900.

Prof. A. W. REINOLD, F.R.S., Vice-President, in the Chair.

DR. R. A. LEHFELDT read a paper on "Electromotive Force and Osmotic Pressure."

This paper is an attempt to explain a difficulty in the interpretation of the ordinary logarithmic formula for the E.M.F. between a metal and solution, pointed out by the author at the Dover meeting of the British Association. An expression for the E.M.F. of a concentration cell is obtained thermodynamically upon the assumption that the electrolyte is only partially dissociated. A partition is used which is permeable to water, but not to the salt or its ions, and the conclusion follows that the E.M.F. depends not on the osmotic pressure of the metallic ions, but on that of the solution as a whole. A graphical representation is given plotting osmotic pressure against dilution, assuming Boyle's law to hold, and it is shown that the E.M.F. is not proportional to the integral $\int PdV$, but to the converse integral $\int VdP$. Assuming,

further, that the osmotic pressure changes according to Van der Waals's equation, the E.M.F. is greater than that calculated from Boyle's law. If the electrolytic solution pressure is calculated from the integral $\int PdV$ it comes

out 10¹⁰ atmospheres, but if from the converse integral the value obtained is about 20,000 atmospheres. A comparison between actual E.M.F.'s and those derived from the equation given by the author should afford, if the formula is correctly deduced from the assumptions made, a measure of how far the osmotic pressure deviates from that indicated by Boyle's law. Experiments upon concentration cells have been made by Helmholtz, Wright and Thomson, Moser, Lussana and Goodwin, but as their work was performed upon cells with migration of ions, the calculation of the osmotic pressure is rendered uncertain by the introduction of the transference ratio. Accordingly the author has measured the E.M.F.'s of cells without migration, using zinc as electrodes, and chloride and sulphate of zinc as salts. The E.M.F. was measured by the compensation method, using a post office box through which a current was sent by an accumulator. The accumulator kept up a constant potential difference, and was standardised daily by means of a Clarke cell. The experimental results agree with the calculated over the range centi- to deci-normal, showing that the deviation from the value given by the logarithmic formula is accounted for by the incomplete dissociation of the salts. The osmotic pressures are then calculated from the E.M.F.'s, and the values of PV plotted. They show irregularities due to the combined effect of the decreasing dissociation of the salt, and the increasing departure from Boyle's law. Dividing the product PV by van't Hoff's factor, determined from conductivity, values are obtained showing variations similar to those observed in the behaviour of gases when subjected to high pressure.

MR. WRETHAM said there was one form of membrane which is quite permeable to water, and yet does not allow either salts or the ions to get through. He referred to the free surface of the solution itself. The water being volatile can get out, but the salt cannot.

DR. DONNAN said the author seemed to have discovered things well known; for instance, the integral $\int VdP$ is generally taken as proportional to E.M.F. He expressed his interest in the explanation of the difficulty in the logarithmic formula.

DR. LEHFELDT, in reply, said Goodwin had used the integral $\int VdP$, but had not made any numerical calculations by means of it.

MR. R. J. SOWTER read a paper on "Astigmatic Lenses."

An astigmatic lens is one which so acts on rays of light falling on it as to produce in general two focal lines in the refracted ray system. A lens derived from a quadric surface is the general elementary type of astigmatic lens, and in the paper an ellipsoidal lens is selected and considered. The focal lines are parallel to the elliptic axes, and

correspond to the lens powers in these directions. These powers are proportional to the inverse squares of the axes. A curve drawn through all points on a lens where the material thickness is constant may be said to determine a natural aperture for that lens. A method of natural apertures is employed to establish the various relations set out in the paper. An ellipse is the natural aperture for an ellipsoidal lens, a circle for a spherical lens, and an infinitely long rectangle for a cylindrical lens. It is shown that two cylindrical lenses crossed at right angles are equivalent to an ellipsoidal lens, and the power of the combination in any direction is the same as that of the ellipsoidal lens in that direction. It is also shown that two obliquely crossed cylindrical lenses are equivalent to an ellipsoidal lens, or to two cylindrical lenses of definite powers crossed at right angles, or to a cylindrical and a spherical lens, for a spherical lens may be replaced by two equal cylindrical lenses crossed at right angles.

Prof. S. P. THOMPSON said he had never seen the treatment of an ellipsoidal lens before, although the extreme case of a paraboloidal lens had been considered. The author's method was, so far as he knew, new, and would be very convenient to work with.

Mr. A. CAMPBELL then read the following papers:—

(a). "On a Phase-turning Apparatus for Use with Electrostatic Voltmeters."

Electrostatic voltmeters are particularly insensitive at the lower parts of their ranges, the divisions closing in very much towards the zero point. When measurements of small direct-current potential differences have to be made, it is an easy matter to add to the voltage to be measured a constant voltage large enough to bring the deflection to an open part of the scale. If the small voltage to be measured is an alternating one, it is necessary that the auxiliary voltage should alternate with the same frequency, and be in phase with it. The apparatus described enables the phase of the auxiliary voltage to be turned until it agrees with the one to be measured. The phase difference referred to is not the time lag, but the angle whose cosine is the power factor, and may be called the power lag. The method is to get two independent equal voltages, U_1 and U_2 , differing in power phase by $\pi/2$, and to add together suitable fractions of these, such as $U_1 \sin \phi$, $U_2 \cos \phi$. The resultant is equal to U_1 , but with the power phase turned through ϕ . The unknown small voltage is connected in series with an auxiliary voltage and a voltmeter, and the phase of the latter voltage is turned until the maximum deflection is obtained.

(b). "On a Method of Measuring Power in Alternating Current Circuits."

The circuit in which the power is to be measured is connected in series across the supply circuit with a small non-inductive resistance. By means of a transformer the small voltage on this resistance may be transformed into one whose power phase is π behind the voltage on the resistance. This is added to the voltage on the circuit to be measured and then reversed, and added again. The difference of the squares of these effective resultants is shown to be equal to a constant into the power to be measured. If there is any direct current it must be measured separately by a Weston voltmeter or other suitable instrument.

(c). "Note on obtaining Alternating Currents and Voltages in the same Phase for Fictitious Loads."

When testing instruments for the measurement of large amounts of electrical power or energy, it is usually desirable to do so by means of fictitious loads, *i.e.*, by applying to the instrument under test current and potential difference representing the required load. In order to obtain a fictitious non-inductive load with alternating currents, the potential difference and current should be in the same phase. The current for the instrument under test is got by means of a transformer worked on a hundred-volt circuit. The potential difference in the same phase is got by allowing the current to flow through a non-inductive

resistance, and increasing the voltage at the ends of the resistance to the required amount by means of another transformer.

The Society then adjourned until November 23rd.

NOTICES OF BOOKS.

Handbook of Spectroscopy. (Handbuch der Spectroscopie).

By H. KAYSER, Professor of Physics at the Bonn University. Vol. I. Leipzig: S. Hirzel. 1900. Pp. 781.

For the last ten years Prof. Kayser has devoted a large portion of his time to the compilation of his great work on Spectroscopy, the first volume of which is now before us. In this volume the author has dealt with the subject up to the beginning of 1899, and there remains a large amount of work to complete his record of all that has been written and done since then up to the present time.

This volume is divided into six chapters, each of which is subdivided into a number of sections. Chapter I. deals generally with the science of spectroscopy, beginning with the work of Newton, Herschel, Wollaston, Fraunhofer, and many other distinguished workers. The subject is so vast that we can only briefly follow the author in his history of the growth of the science; emission and absorption spectra, Brewster's three-colour theory, the theory of heat rays, phosphorescence and fluorescence, the spectra of gases, and spectrophotography are but a few of the important points here fully discussed.

Chapter II. is on the production of luminous vapour, subdivided into sections on flames, the electric arc, and the electric discharge. Chapter III. is an important one, and is devoted to prisms; the theory of the prism is fully gone into, in the first section, and its construction in the second; the comparative advantages of and improvements in various prisms are given, including those made from such substances as fluorite, sylvine, rock salt, quartz, and calc spar. We next come to diffraction gratings, and then, in Chapter V., to the construction of the spectroscope, and of spectroscopic apparatus. In this particular branch of the subject we are almost overwhelmed with the number of workers; nearly every chemist and physicist of note seems to have added his quota to the development of the still-growing instrument, while those who cannot lay claim to any improvements have, on the other hand, made excellent use of the instruments as they stood.

Chapter VI. and last is on spectroscopic measurements, and is divided into two principal parts, *viz.*, absolute measurements and relative measurements. This subject is one of the greatest importance, as by its means the results obtained by different authorities can be compared together, and new results criticised and tabulated.

Prof. Kayser is an acknowledged authority on this subject, and the excellent work he has just given to us will be received with the appreciation it deserves. His numerous publications on the spectra of the elements are widely known and universally accepted as standard works. It is no light matter to undertake so thorough a history of spectroscopy, and though the work done and published up to within a year or two may be looked upon as settled, and not likely to require much reconsideration, the work that is now going on is enough to prevent any book being actually up to date when published, as even while it is passing through the press something new is almost bound to be announced.

Besides a full table of contents, this volume has two good indices, one of author's names and the other for subject matter. It is also embellished with 251 illustrations.

Partial Synthesis of Laudanosine.—Amé Pictet and B. Athanasesco.—Laudanosine, $C_{21}H_{27}NO_4$, one of the least abundant alkaloids contained in opium, was prepared from another opium alkaloid, papaverine, $C_{20}H_{21}NO_4$. This partial synthesis fixes the composition, that of papaverine having been already established by M. Goldschmidt.—*Comptes Rendus*, cxxxi, No. 17.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

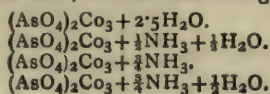
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 17, October 22, 1900.

Diagnoses of Gaseous Supersaturations, of a Chemical and Physical Order.—M. Berthelot.—The author's experiments, which are fully described, establish the fact that oxygen, though susceptible of existing dissolved to a considerable extent in mixtures of hydrogen peroxide and permanganate of potash, really is present in a state of unstable combination. When in the form of hydrogen peroxide, the peroxide is capable of being violently decomposed, with evolution of a considerable quantity of heat; it being, in fact, a chemical supersaturation.

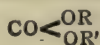
Origin of Atmospheric Hydrogen.—Armand Gautier.—The various phenomena examined by the author seem to point to the fact that the hydrogen present in the air is originally derived from the water: the water reacting on terrestrial substances at a remote period and causing the hydrogen to accumulate. This, however, apparently is only one of the origins of atmospheric hydrogen; the second origin seems to be the residue left in the air, at the moment of the formation of rain water, by the combustion of this hydrogen gas in presence of excess of oxygen, nitrogen, carbonic acid gas, and various vapours.

Index of Refraction and Dispersion of Bromine.—Ch. Rivière.—The physical constants of bromine have been little studied, partly on account of the extreme care necessary in the preparation of pure bromine and also because of the difficulty of manipulation of this substance. Various contradictory numbers have been published. The author examines these numbers afresh, with the aid of improved apparatus. The numbers published show an extraordinary dispersive power; between lines A and D at 20° C. this power is 0.037 as compared with 0.016 for flint and 0.030 for carbon disulphide. The bromine used in these experiments was prepared by the action of sulphuric acid on a mixture of pure bromide and bromate of potassium, then washed with a large quantity of water and dried with phosphoric anhydride.

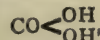
Ammoniacal Arsenates of Cobalt.—O. Ducru.—If a solution of cobalt rich in ammoniacal salts and containing a sufficient proportion of free ammonia, is added to arsenic acid or a double arseniate, a voluminous gelatinous precipitate comes down of a violet-blue colour. If this is kept on the water-bath, the precipitate gradually becomes modified, contracts, and changes to a dark red body, the microscopic examination of which shows it to be completely crystallised. These compounds are the ammoniacal arsenates of cobalt, and it is found that cobalt forms three distinct ammoniacal arsenates, derived from erythrine by the displacement of water by ammonia, molecule for molecule; the four salts being—



A General Method of Preparation of Mixed Carbonic Ethers of the Phenols and the Alcohols.—E. Barral.—The mixed phenolic-alcoholic carbonates—



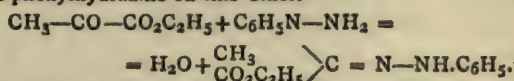
are the ethers of carbonic acid—



in which the atoms of hydrogen have been replaced, one by the phenolic radicle R and the other by the alcoholic

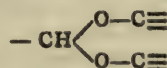
radicle R'. All the rational methods for the preparation of these substances fail, the author showing that all the difficulties arise from the easy formation of the neutral alcoholic and phenolic carbonates, $\text{CO}(\text{OR})_2$ and $\text{CO}(\text{OR})_2$. He therefore decomposes the chlorocarbonates under the influence of alcoholates or phenates, very unstable bodies, which act as caustic alkalis.

Stereochemistry of Nitrogen. The Stereo-isomeric Hydrazones of Ethyl Pyruvate.—L. J. Simon.—The author succeeds in obtaining under two stereo-isomeric forms the hydrazone of ethyl pyruvate, by the direct action of phenylhydrazine on this ether.

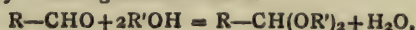


The molecular weight of this substance and the estimation of carbon, hydrogen, and nitrogen, show it to have the above composition.

Acetals of Monovalent Alcohols.—Marcel Delépine.—The author examines several derivative containing the group—



called the formals and the acetals, prepared respectively from formic and acetic anhydrides. He calculates the thermic capacity of their generative action—



in order to establish the nature of the variations in the heats of combustion and of formation by the passage from one form to the other.

Direct Nitration in the Fatty Series.—L. Bouveault and M. Wahl.—By the nitration of ethyl dimethyl acrylate with fuming nitric acid, the author succeeds in preparing a substance of formula $\text{C}_7\text{H}_{11}\text{NO}_4$, named ethyl nitro-dimethyl acrylate. This is a clear yellow liquid, of density 1.1384 and agreeable odour. When the alcoholic solution of this substance is treated with alcoholic potash the potassium salt is formed, $\text{C}_7\text{H}_{10}\text{NO}_4\text{K}$. A solution of this can be decomposed by dilute hydrochloric acid, when a dark heavy oil appears, of formula $\text{C}_7\text{H}_{11}\text{NO}_4$. This compound is isomeric with ethyl dimethyl acrylate. It boils at a lower temperature, 104°–105°, and has density 1.1279, besides being colourless when pure.

Messrs. A. Gallenkamp and Co.—This firm has recently placed on the market an improved form of balance for scientific purposes, of the highest accuracy with constant sensibility. The great drawback in all analytical balances at present in use is, that within the limit of the maximum weight-charge for which they are constructed, they become less and less sensitive with the increase in the charge; the cause of this is in the bending of the beam, by which the end knife-edges are gradually brought below the plane in which all three should be. To eliminate such errors Messrs. Gallenkamp have constructed a new beam, model 1900, the end supports of which are outside the knife-edges; they claim that this construction is all-important, as it gives absolute rigidity to the beam.

Notes on the Estimation of Boric Acid.—C. Montemartini.—Of all the methods proposed for the estimation of boric acid Gooch's method is the only one giving exact results. It consists of liberating the boric acid by means of nitric or acetic acid, and then transforming it into methylic ether. This latter is collected on a weighed quantity of lime, dried, calcined, and reweighed; the increase of weight is due to the boric acid held. Rosenblad's method is not a good one, neither is Thadéeff's. This latter is very complicated and inconvenient, and does not give anything like such good results as Gooch's method.—*Gazz. Chim. Ital.*, p. 344.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Aniline Dyes and Colours.—A correspondent asks for the title and price of the most exhaustive and modern manual on the manufacture of aniline dyes and colours, containing fullest directions as to the various manufacturing processes, chemicals, materials, machinery, &c., to be employed in order to attain the best possible results. The work may be either in English or German as long as the instructions are comprehensive and complete.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Society of Arts, 8. Opening Address of the 147th Session, by Sir John Evans, K.C.B., F.R.S. Microscopical, 7.30. Exhibition of Slides illustrating the Structure of Shells.

FRIDAY, 23rd.—Physical, 5. "The Anomalous Dispersion of Carbon," by Prof. R. W. Wood. "The Liquefaction of Hydrogen," by M. W. Traversa. "Refraction of Sound by Wind," by Dr. E. H. Barton.

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The arrangements for the Examinations depend upon the number of candidates. Candidates for the Intermediate Examination may be required to present themselves from Tuesday, Jan. 22, to Friday, Jan. 25, 1901. Notice will be given to all Candidates whose applications for examination are received and accepted by the Council not later than Monday, Dec. 3, 1900, on which day the examination lists will be closed.

By Order of the Council,

RICHARD B. PILCHER, Registrar.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2139.

THE ACTION OF AMMONIA UPON FERROUS CHLORIDE AND BROMIDE.

By GILBERT J. FOWLER, M.Sc.

THE experiments to be described were made in the course of a research on the preparation and properties of iron nitride, and their general results are given in a paper on that compound. The details, however, seemed to be of sufficient interest to publish in a separate note.

Although the action of ammonia upon ferrous chloride was not found to be the best method for preparing nitride of iron, yet a number of experiments were made with the view of gaining a more certain knowledge of the action of ammonia in this case, and to determine especially whether any hydrazine derivatives were formed. The ferrous chloride was prepared by heating iron wire to redness in a current of hydrogen chloride, the crystalline product obtained being freed from intermixed metallic iron by means of a magnet.

In the cold, ammonia is very rapidly absorbed by ferrous chloride, the crystals swelling up to a white powdery mass with evolution of heat, the temperature rising to above 40° C. On introducing ferrous chloride into ammonia gas over mercury, the ammonia is instantaneously absorbed, the experiment being a striking one for lecture illustration. Quantitative experiment showed that from 5 to 6 molecules of ammonia are thus taken up. On exposure to the air the white mass rapidly turns brown, with formation of hydrate of iron. On heating the white substance to the boiling-point of alcohol, in a tube connected with a manometer, no appreciable amount of ammonia was evolved; at 100°, however, a rapid evolution of this gas took place.

In order to investigate the action of ammonia upon ferrous chloride at higher temperatures, the ferrous chloride was spread, in a thin layer, in a hard glass tube contained in a Lothar-Meyer furnace, giving temperatures which can be kept regular up to 500°. Ammonia gas was first of all passed through at the ordinary temperature till all the air was expelled. The temperature was then raised, and at 160° ammonia came off very rapidly from the white compound of ammonia and ferrous chloride, formed in the cold, but no gas unabsorbed by hydrochloric acid was obtained. At 300° this ammonia had not ceased coming off, but no sublimation of ammonium chloride was noticed.

At a temperature above 300°, but below the melting-point of lead, 335°, the mass began to melt and darken, a large amount of ammonium chloride was formed, marking a decomposition of the ferrous chloride, but very little unabsorbed gas was evolved. At the melting-point of zinc, 433°, a small amount of gas was found to be unabsorbed by the acid in the nitrometer connected with the apparatus. On allowing the apparatus to cool, complete absorption of the ammonia took place in the nitrometer, showing that the gas collected was not due to any air having diffused into the apparatus. The temperature was kept low in this experiment, in order better to observe the formation of products intermediate between ferrous chloride and nitride of iron, which, according to Fremy, is the final product of the reaction. The gas evolved was found to be non-inflammable, and therefore was not hydrogen, and since, as mentioned above, it was not air, would seem therefore to consist of nitrogen, produced in the course of the reaction. The solid residue in the tube consisted partly of unaltered ferrous chloride, as, on allowing to cool, more ammonia was absorbed. On treating the mass with dilute sulphuric acid, and rapidly

pouring off the solution obtained, a residue of less soluble substance was left, having all the external properties of nitride of iron prepared by other methods, and slowly soluble in sulphuric acid with formation of ferrous and ammonium sulphates. Nitride of iron is therefore formed by the action of ammonia upon ferrous chloride at the temperature of molten lead. It is impossible definitely to decide whether an intermediate compound, e.g., FeNH_2Cl , is formed at this temperature, as a mixture is obtained of nitride of iron, ammonium chloride, and unaltered ferrous chloride, which latter absorbs ammonia. The solution obtained by treating the contents of the tube with sulphuric acid, as described above, was tested for hydrazine by distilling with caustic soda, continuing as long as the contents of the distilling flask were liquid, and testing the distillate with Fehling's solution. A very slight reduction, obtained in one case, was found to be due to a trace of ferrous salt carried over.

In another case the sublimate alone was tested by precipitating with potash, filtering, and boiling with Fehling's solution. No reaction, however, was obtained.

When ferrous chloride is heated with ammonia, the latter is first absorbed to form the molecular compound mentioned above. On further heating, reduction of the ferrous chloride takes place, resulting in the formation of ammonium chloride, nitride of iron, and a small quantity of nitrogen. To prepare the nitride in quantity by this method, a temperature of about 600° appears to be necessary.

Ferrous bromide was prepared and similarly treated. The temperature of reaction was not sensibly lower, and the products of reaction were analogous. In one case, where ferrous bromide was used, the products of the reaction, at about 350° C., were dissolved in acid and reduced with zinc, previously to distillation with caustic soda, in order to prevent oxidation of any hydrazine, by means of the ferric hydrate formed. No trace of reduction of the Fehling's solution was obtained in the distillate from caustic soda.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART V.

By HARRY BREARLEY.

(Continued from p. 199):

SILICON.

THE items are arranged, as sharply as possible, under the following heads:—

- I. THE ESTIMATION OF SILICON IN METALS.
 - a. Iron and Steel.
 - b. Alloys.
 - c. Aluminium.
- II. THE ESTIMATION OF SILICA IN REFRACTORY MATERIALS.
- III. THE ESTIMATION OF SILICA IN SLAGS AND SILICATES.
- IV. MISCELLANEOUS.

I. THE ESTIMATION OF SILICON IN METALS.

I.a. In Iron and Steel.—

665. ABEL (C. N., vi., 124; and FORBES (C. N., xvi., 105).—Pig dissolved in HCl, evaporated; Si dissolved from the graphite with KHO, and recovered again by evaporation with HCl.
666. ALLEN (C. N., xxix., 91).—Similar to Abel. When iron is dissolved in HCl or H_2SO_4 , the silicon is not liberated as SiO_2 , but as leucon. For particulars of leucon see Wöhler (C. N., viii., 171 and 182).

667. SCHNEIDER (*Y. C. S.*, lxvi., ii., 162).—Dissolve in HCl, and evaporate with H_2SO_4 to dehydrate the silica.
668. BLUM (*C. N.*, liii., 300).—Dissolve in HCl and evaporate. The addition of $(\text{NH}_4)\text{Cl}$ increases the rapidity of evaporation.
669. RUBRICIUS (*Y. I. S. I.*, 1893, i., 411).—Dissolve pig in small excess of HCl, filter at once, ignite residue with KNO_3 , boil with $(\text{NH}_4)\text{Cl}$, and collect the hydrated silica.
670. SCHNEIDER (*Y. I. S. I.*, 1893, ii., 532).—Processes of evaporation with HCl, or solution of the baked residue in HCl, are erroneous. SiO_2 is markedly soluble in HCl: it should be dehydrated by evaporation with H_2SO_4 .
671. DROWN (*C. N.*, xlii., 299).—On dissolving Fe in HCl, the less Si passes into solution the stronger the acid. High Si irons may be fused with KHSO_4 , digested with HCl, and SiO_2 filtered off.
672. ALLEN (*C. N.*, xl., 65).—As leucon, the form in which Si is liberated from iron, is soluble in water, no fixed proportion of silicon invariably passes into solution. Means of distinguishing leucon given.
673. EGGERTZ (*C. N.*, xviii., 100 and 115).—Dissolve Fe with Br or I and water at 0°C , and separate SiO_2 from the slag with $\text{Na}_2\text{CO}_3\text{Aq}$. If iron is dissolved in HCl, very little Si passes into solution; if HNO_3 , much. By dissolving in H_2SO_4 and evaporating to SO_3 fumes, nearly all the SiO_2 is separated.
674. EGGERTZ (*C. N.*, xviii., 232).—Dissolve in H_2SO_4 ; add HNO_3 , evaporate, re-dissolve in HCl, and collect SiO_2 .
675. PIESSE (*C. N.*, xxix., 57).—Effect solution with nitro-sulphuric and evaporate at 100°C .
676. DROWN (*C. N.*, xl., 40).—Decompose with nitro-sulphuric and evaporate to SO_3 fumes. By treating iron with HCl, H_2SO_4 , and HNO_3 , the Si passing into solution is in the order named.
677. DROWN (*C. N.*, lx., 20).—Nitric acid of sp. gr. 1.135 dissolves pig-iron completely without causing any SiO_2 to separate.
678. LANGMUIR (*C. N.*, lxxix., 216).—To effect a more complete dehydration in (676) a strap is passed round the beaker, and the solution kept in motion over the naked flame.
679. JONES (*C. N.*, lx., 79).—The nitro-sulphuric solution is evaporated in three to five minutes by two flames, one of which impinges on the surface of the liquid.
680. AUCHY (*Y. I. S. I.*, 1898, ii., 559); and CROBAUGH (*Y. I. S. I.*, 1899, ii., 484).—To use a mixture of aqua regia and H_2SO_4 is more accurate and convenient than nitrosulphuric acid.
681. JÜPTNER (*Y. I. S. I.*, 1884, 603).—Comparison of various methods. Drown's process (676) gives good results in the presence of Ti. Estimating SiO_2 by volatilisation with HF is objectionable.
682. DUDLEY (*C. N.*, lxx., 186).—Silica dehydrated by evaporation to SO_3 fumes is partially re-dissolved when allowed to stand in the acid solution.
683. FORD (*Y. S. C. I.*, 1893, 1061).—Silica dehydrated by process 676 is not re-dissolved as Dudley suggests.
684. JERVIS (*C. N.*, lxxviii., 63).—Dissolve in dilute nitro-sulphuric acid, and deliver water on to the dry hot mass; this avoids cooling cracks, and no SiO_2 is re-dissolved on standing.
685. TROILIUS (*C. N.*, xlv., 310).—Dissolve in dilute H_2SO_4 , evaporate to SO_3 , dissolve separated salt in HCl, filter off SiO_2 , and wash with HNO_3 .
686. TURNER (*C. N.*, lvi., 49).—Phosphoric irons evaporated with H_2SO_4 may give a white, but still impure, SiO_2 . When evaporated with aqua regia, the colour of the SiO_2 is an indication of purity.
687. TOSH (*C. N.*, xvii., 168).—Evaporate aqua regia solution, fuse SiO_2 with KNO_3 , and evaporate the dissolved melt with HCl.
688. MORGAN (*C. N.*, lvi., 221 and 244).—Evaporate aqua regia solution to syrupy condition only; the SiO_2 is free from phosphide of iron with highly phosphatic irons.
689. PARRY and MORGAN (*C. N.*, lxvii., 149).—As Morgan; but evaporate to dryness and then re-evaporate HCl solution to skin; fuse with KHSO_4 , to separate iron phosphide. H_2SO_4 is essential when SiO_2 is to be volatilised with HF.
690. LIEBRICH (*Y. I. S. I.*, 1896, i., 532).—After evaporating acid solution of the pig, ignite the filtered residue with KHSO_4 to burn off graphite and separate Fe and Ti.
691. LECLERC (*Y. C. S.*, lx., 1397).—Dissolve in nitro-hydrochloric acid, expel HNO_3 , and evaporate after addition of ammonium chloride to prevent Mn contaminating SiO_2 , and KCl to prevent the decomposition of Fe_2Cl_6 .
692. TURNER (*Y. C. S.*, xlv., 260).—Various methods compared. Dissolving in HCl or nitro-sulphuric untrustworthy for Si pigs or Si speigels.
693. MORGAN (*C. N.*, lvi., 83).—Roast finely-divided sample in the muffle to oxidise Si, digest with HCl, and collect SiO_2 .
694. WATTS (*C. N.*, xlv., 279); and TURNER (*C. N.*, xlix., 233).—Volatilise Si along with iron in Cl at red heat, collect SiCl_4 in H_2O , and evaporate for SiO_2 . Any slag or cinder remains with the carbon in the boat. (See 673 and 748).
695. KONINCK (*Y. I. S. I.*, 1894, i., 614).—The solution of the iron is precipitated by $(\text{NH}_4)\text{HO}$ or acetate, and the ignited precipitate heated in HCl gas; SiO_2 (and Al_2O_3) remain in the boat.

I.b. In Alloys.—

696. CLERC (*Y. I. S. I.*, 1889, ii., 479).—Dissolve powdered ferro-silicon in bromised HCl, evaporate one-half, and collect SiO_2 ; the error is insignificant.
697. HOGG (*C. N.*, lxvii., 27).—Boiled finely-powdered Fe-Si or Si spiegel with nitro-hydrochloric acid, filter, and ignite to SiO_2 . Only 0.1 to 0.3 per cent Si passes into solution when dealing with 10 to 15 per cent alloys.
698. PLATT (*Y. I. S. I.*, 1893, i., 411).—As Hogg, but adds H_2SO_4 containing SO_3 to render Si insoluble.
699. MURRAY and MAURY (*Y. C. S.*, lxxii., ii., 599).—Decompose silico-spiegel with $\text{HCl} + \text{H}_2\text{SO}_4$, evaporate to SO_3 fumes, and volatilise SiO_2 with HF. Done in half an hour.
700. WILLIAMS (*Y. I. S. I.*, 1889, i., 397).—Fuse Fe-Si with Na_2CO_3 and evaporate melt with HCl; the SiO_2 is pure.
701. ZIEGLER (*C. N.*, lxvi., 295).—Fuse Fe-Si or Fe-Cr with KHSO_4 , dissolve melt, and collect SiO_2 .
702. DONATH and HALLSIE (*Y. I. S. I.*, 1897, ii., 488).—Ferro-silicons cannot be dissolved by HCl, HNO_3 , or aqua regia. Fuse with Na_2CO_3 and NaNO_3 .
703. BORNTREGER (*Y. C. S.*, lxxvi., ii., 695).—Silicon is analysed by dissolving in potash; the impurities, Al_2O_3 , Fe_2O_3 , and Fe-Si, are left undissolved.
704. TATE (*C. N.*, lxxx., 235).—Fuse FeCr with Na_2O_2 , evaporate the neutralised melt, and heat with H_2SO_4 to fuming; finally, vaporise SiO_2 with HF. Much of the Cr escapes during the H_2SO_4 treatment as chlorochromic acid.
705. MOISSAN (*Y. C. S.*, lxvi., ii., 43).—Carbide of silicon (carborundum) is decomposed by fusion with KHO. KNO_3 and KClO_3 have no effect on it, nor has any mixture of acids.
705. MUHLHAUSER (*Y. S. C. I.*, 1894, 402).—Uses the elutriated powder of carborundum, and decomposes with KNaHO . Estimate the carbon by burning a like powder with PbCrO_4 .

* Gives a method of estimating graphite and combined carbon in ferro-silicons which should have been noticed under "Carbon."

707. SCHÜTZENBERGER (Z. C. S., lxii., 1050).—Carborundum as Moissan. The volatilisation of the Si in a current of chlorine is not complete.

I.c. In Aluminium.—

708. HUNT, CLAPP, and HANDY (C. N., lxx., 223).—Si exists in Al in the graphitoid and combined form. Dissolve in nitro-hydrochloric, evaporate with H_2SO_4 , and collect Si+ SiO_2 . SiO_2 cannot be estimated by volatilisation. Si is also partially oxidised, therefore fuse with Na_2CO_3 , dissolve in HCl, evaporate with H_2SO_4 , and weigh total Si as SiO_2 .

709. HANDY (Z. C. S., lxxii., ii., 191).—To determine graphitic Si decompose Al with HCl+HF, filter through paraffin-coated funnel, fuse with Na_2CO_3 , and estimate as SiO_2 .

710. REGELSBERGER (Z. C. S., lxxiv., ii., 48).—Decompose with aqua regia + H_2SO_4 , drive off HNO_3 , collect Si+ SiO_2 , and evaporate with HF; loss = SiO_2 . Evaporate residue with HF+ HNO_3 ; loss of weight = Si. (See 708 and 761).

711. MOISSAN (Z. C. S., lxx., ii., 339).—Decompose with HCl, fuse insoluble and add to main solution; evaporate at $125^\circ C.$ to separate SiO_2 .

712. SIBBERS (Z. C. S., lxxiv., ii., 409).—On dissolving Al in HCl appreciable amounts of Si are volatilised. Dissolve in current of H which on ignition at the delivery tube deposits SiO_2 .

713. GONTHIERE (Z. S. C. I., 1896, 83).—Dissolve in nitro-hydrochloric and proceed as for steels, taking no account of graphitic Si.

714. ANON. (Z. I. S. I., 1892, i., 491).—Dissolve in KHO, acidulate with HCl, evaporate, and collect SiO_2 .

(To be continued).

ON THE ESTIMATION OF MANGANESE AS PYROPHOSPHATE.

By WILHELM BÖTTGER.

THE want of precise instructions on the use of Wolcott Gibbs's method (Zeits. f. Analyt. Chem., [6], v., 174), the partial contradictions as to certain of its details (Fresenius, "Quant. Analyse," 259; Kessler, Zeitsch. f. Anal. Chem., xxxiii., 8), and the want of success of the method when in unpractised hands, have decided the author to closely examine this method of quantitative estimation. Although the conditions necessary for the success of the operation have figured for some months past in Autenrieth's work on analysis, the results of his experiments have not yet been published.

In Miller and Kiliani's book on Chemical Analysis, as well as in that of Zimmermann, we read that a neutral solution of a salt of manganese should be treated with an excess of disodic phosphate, and the precipitate of $Mn_2(PO_4)_2$ obtained dissolved in a few drops of hydrochloric acid. The liquid should then be brought to boiling, an excess of ammonia added, and then heated on the water-bath until the double phosphate of ammonium and manganese, deposited in the amorphous state, becomes transformed into crystalline leaflets. Autenrieth's instructions differ from the above in the use of an ammoniacal salt and the absence of acid.

From the point of view of equilibrium in phenomena of supersaturation, the formation of a substance in the solid state takes place in any system when the concentration exceeds the solubility at any given temperature. If the dissolved material undergoes a modification (hydration, polymerisation, ionisation, &c.), the solubility, in the strictest sense, is in relation to the part which remains intact. The apparent solubility includes the modified portion. The concentration of the material is always connected by definite relations with that of the products of transformation. On bringing these two relationships together, that is to say, the one above mentioned, and

that which exists between the non-modified portion and the solid material, we can connect the definition of solubility with that of the concentration of the products of transformation. If we do this, particularly in the case of electrolytic decomposition into ions, we arrive at the conclusion that the product of the concentration of the ions under given conditions, and in presence of the solid phase, possesses a definite value.

The analytical expression (Ostwald, Wissenschaftliche Grundlage der Analytischen Chemie, ii., Aufl. 70; Grundriss der Allgemeinen Chemie, iii., Aufl. 427) of this will be—

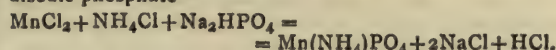
$$A^m \times B^n = \text{const.},$$

where A and B represent the concentration of the ions, and m and n the respective figures of the combining weights of the ions which take part in the transformation.

In the case in question where the manganese is precipitated in the state of $Mn(NH_4)PO_4$, it is necessary to bring about such conditions that the concentration of the ions PO_4^{3-} and NH_4^+ may be as great as possible.

The increase in the concentration of the ion NH_4^+ before the addition of the phosphate is effected by the use of an ammoniacal salt, which, like other normal salts, is capable of dissociation. As solutions of ammonia contain few NH_4^+ ions, it is not necessary to add a large quantity; besides that, $Mn(OH)_2$, which is then converted into phosphate, is easily formed. There is, however, a disadvantage in the fact that $Mn(OH)_2$ in absorbing oxygen passes into the state of $(MnOH)_3$, which completely destroys the success of the analysis.

The best means of preventing this annoyance consists in introducing into the neutral solution a quantity of ammoniacal salt* representing five to ten times the molecular quantity, boiling the liquid, and then adding an excess of disodic phosphate—



The free acid which is thus formed, and which prevents complete precipitation, is neutralised with a little ammonia. It is necessary to heat until the amorphous substance is completely transformed into a crystalline precipitate.

By examining the accompanying table, where the results of different analyses made with sulphate of ammonium and manganese are given, we can see that the method can be used perfectly well in all ordinary cases. One cause of error is due to the slight solubility of the precipitate in water, which can be shown by adding a little nitrate of silver to the filtrate.

No.	$Mn_2P_2O_7$ used. Grms.	Quantity found.	Per cent.	Observations.
1.	0.4449	0.4452	100.1	5 grms. of sulphate of ammonia, 25 c.c. of solution of disodic phosphate,* 10 c.c. of concentrated ammonia.
2.	0.4410	0.4401	99.8	
3.	0.4355	0.4371	100.3	
4.	0.4423	0.4417	99.9	
5.	0.4369	0.4383	100.3	
6.	0.4394	0.4412	100.4	Like 1 to 5, only 5 c.c. of dilute ammonia (double normal).
7.	0.4428	0.4432	100.1	
8.	0.4358	0.4351	99.8	
9.	0.4370	0.4363	99.8	3.2 grms. sulphate of ammonia, 25 c.c. Na_2HPO_4 solution, 10 c.c. dilute ammonia.
10.	0.4397	0.4388	99.7	Like 9, but 1.6 grms. of sulphate of ammonia.
11.	0.4362	0.4327	99.2	5 grms. sulphate of ammonia, with 10 c.c. of concentrated ammonia.
12.	0.4362	0.4327	99.2	10 cc. of dilute ammonia; precipitate washed with hot water.

* The solution of Na_2HPO_4 was about 12 per cent.

* The use of an ammoniacal salt has the advantage of increasing the concentration of the NH_4^+ ion, and, by preventing the dissociation of the ammonia, limiting the concentration of the HO ions.

Thus, as shown by analysis 11 and 12, the washing of the precipitate with warm water increases the error. It is therefore preferable to moisten the substance with slightly ammoniacal cold water.

If we take care to wash the phosphate until the filtrate leaves no residue when evaporated down and heated to redness on a strip of platinum, we can eliminate the ammoniacal salt by calcining over a blowpipe flame. The author has never found manganese in the residue from the evaporation of the wash-waters, on dissolving it with salt-petre and carbonate of soda. He concludes with the remark, that even when placed in inexperienced hands the method in question has been proved to be of advantage.—*Berichte*, xxxiii., p. 1019.

THE PLASTICITY OF SOLID BODIES, AND ITS CONNECTION WITH THE FORMATION OF ROCKS.

By W. SPRING.

FARADAY showed, in the year 1850, that two fragments of ice, pressed one against the other, united with greater ease as their temperature approached zero. This fact does not at first appear to be of any great importance, but soon—owing to the ingenuity of Tyndall—it soon led to the explanation of the formation of glaciers; his experiments are too well known to require further mention; suffice it to say that they established the fact that compression alone of the snow was enough to form those immense glaciers which cover many mountain tops and the polar regions.

It may be asked if this phenomenon is peculiar to ice, and whether other bodies do not also possess the property of joining together under pressure. The results of numerous observations show that such a property is to be found in different degrees in certain substances; it is very slight in some bodies, more pronounced in others, and is distinct in a few substances only.

The task of verifying the existence of this property appeared to be of great interest, inasmuch as important light would be thrown on several questions concerning the physical properties of solids in general, and more particularly on the formation of sedimentary rocks from the gravels, sands, and clays from which they are derived.

The manner in which the hardening of these rocks is effected is still obscure. Most of them appear to want in matter capable of acting as a cement uniting the agglutinated particles. How, then, can the coherence have been caused in so complete a manner in substances which were originally non-coherent? Might it not be by a process similar to that which formed glaciers? and, if so, would not our ancient rocks, with their folds, fractures, and faults, be found, from the point of view of their formation, in the image of our modern glaciers?

To make certain whether solids, other than ice, are endowed with the property of joining together, it suffices to bring about the conditions in which this regelation is produced. These conditions are pressure, temperature, and time. In other words, we must find out whether certain solid particles, unable to join together under ordinary conditions, cannot be made to agglutinate under the influence of a sufficiently great pressure.

We therefore constructed a compressor by which we could attain a pressure of about 10,000 atmospheres, or nearly 70 tons per square inch, in the cold, without any of the material escaping; also another apparatus, capable not only of exerting similar pressures, but also of being heated up to 400° C. at the same time.*

The first experiments showed that all bodies endowed with the property of changing their form under pressure without breaking became as solidly agglutinated as if they had been fused, while those which were not malleable remained pulverulent even under the greatest pressure.

It should be specially noticed that quartz or clayey sands, carbonate of lime in various forms, oxides of iron and alumina, in short the substances which most frequently enter the composition of rocks, are those in which agglutination was non-existent, or at any rate imperfect. The conditions for the solidification of rocks cannot therefore be found exclusively in pressure. It may be mentioned that, if a pressure of 70 tons is insufficient to agglutinate sand, the quartzose rocks must have been solidified by some other force than pressure alone, as 70 tons pressure represents a column of sand 50,000 metres high.

The metals behave in a striking manner; the more malleable they are, the better they agglutinate; they flow under the action of pressure, and grains (filings) are cemented into a solid mass as if they had been fused. It must not be supposed that they could have been fused, for the pressure was never applied by blows, or suddenly, but always very gradually. It was further observed, experimentally, that the rise of temperature was negligible. But if the hypothesis of fusion cannot be entertained to explain this cohesion, we can only attribute it to an inter-diffusion of the molecules in contact, to a sort of inter-solution of the surfaces of the solids. This explanation may appear to be a bold one; it is not difficult, however, to show that it agrees with observed facts.

If there is a true diffusion of the molecules at the surfaces of contact, it follows that the compression of different metals will make an alloy, and not simply a conglomeration of particles, each retaining its individual properties. Experiment has confirmed this supposition in the most complete manner.

By compressing a mixture of tin and copper, both in the form of powder, we obtained bronze; zinc and copper gave brass; copper and antimony furnished a characteristic violet alloy; finally, bismuth, tin, lead, and cadmium, in the proper proportions, formed an alloy which fused in boiling water.

It must be quite understood that, after the first compression of a mixture of the filings of metals, the alloy is only formed at the true surface of contact of the grains. To increase the quantity, the cylinder formed by compression is filed, and the filings compressed again; this is repeated five or six times, when the result is visible to the naked eye.

We must therefore admit that two fragments of solid bodies, of the same or even of different species, brought into absolute contact by the action of sufficient pressure, diffuse one into the other in the same way as a soluble body diffuses in its solvent. In a general way these experiments show that the phenomenon of solution is not subordinate to a state of liquidity of the material; solid bodies dissolve, giving solid solutions. J. H. van't Hoff has arrived at similar conclusions in examining the anomalies shown by the congealing of certain solutions. We must therefore regard solid bodies as having conserved, to a certain point, the molecular mobility characteristic of the fluid state. But even here there remains a notable difference, as liquids are subject to free evaporation, while solids appear to retain all their molecules in a definitely determined space appropriate to their special nature. For example, zinc will evaporate into copper, and vice versa.

If the agglutination of bodies is not only a mechanical act, but if it is rather the consequence of a reciprocal solution of solid bodies, it naturally follows that bodies not soluble in each other will not be joined together by pressure. This is proved to be so by experiment. We know that simply melted lead and zinc are not miscible; they separate one from the other like oil and water; it is

* The description of this apparatus will be found in the *Bulletin de l'Académie Royale de Belgique*, Series 2, vol. xlix., p. 323. Details of the experiments, of which a summary only is given in this article, will be found in the same publication, Series 3, vol. x., p. 204; vol. xviii., p. 23; vol. vi., p. 507; vol. xiii., p. 409; vol. xxx., p. 199;

vol. xxxii., p. 51. See also the *Bulletin de la Société Chimique de Paris*, vol. xli., p. 488; vol. xlvi., p. 299, and the *Zeitschrift für Phys. Chemie*, vol. v., p. 322.

only at high temperatures that the reciprocal solubility of these two metals becomes apparent. Bismuth behaves to zinc in the same way as lead does; now, if we compress, in the cold, a mixture of powdered lead and zinc, or bismuth and zinc, we only obtain an agglomeration softer than before, but still not a homogeneous mass.

Nevertheless, it may be asked whether the junction of solids is not all the same the consequence of the inevitable kneading produced by pressure rather than of a solid solution. The solid grains might well behave like balls of clay which have been worked up and form a mass without diffusion taking any special part in the operation. This can be proved by experiment; it suffices to eliminate the compression, and to make certain whether the solids still join together when all precautions are taken to effect their perfect physical contact simply by superposition. For this purpose accurately made straight sections of cylinders of different metals, such as gold, platinum, silver, copper, zinc, lead, tin, bismuth, &c., were prepared. These cylinders were then placed one on the other in couples, with no other pressure than their own weight. A certain amount of adherence was at once noticed, even in the cold. The temperature was then raised, though it was always kept far below the melting-point (from 200° to 1600° below, according to the metal). The duration of contact varied from three to twelve hours, according to the metal. The result was most surprising; the metals of the same kind were joined together, so as to form but a single mass, and the joint could not even be detected after cleaning the surface in the lathe. The pairs of metals, which were of different kinds, were alloyed the deeper as their malleability was greater. Thus copper and zinc formed a layer of brass a quarter of a millimetre in thickness, while lead and tin were alloyed to a depth of nearly 6 millimetres. Finally, the metals not having the power of dissolving, viz., zinc and lead, zinc and bismuth, only exhibited the commencement of a junction, without having any strength of cohesion at all. But the resemblance between solid and liquid solutions does not stop here. If we mix a solution of potassic saltpetre and chloride of sodium, sodic saltpetre and chloride of potassium are formed, but only in limited quantities; a certain proportion of the reagents appear to become inactive or incapable of doing chemical work. The inverse of this experiment gives the same results. In both cases the stoppage occurs at the same chemical moment, namely, when the force which gives the impulse to one reaction is exactly balanced by that which causes the inverse reaction. This state of chemical equilibrium is also produced when we submit certain solid bodies of different chemical natures to compression. Thus, we first compressed a mixture of dry sulphate of barium and carbonate of sodium; then, as the inverse, a mixture of carbonate of barium and sulphate of sodium. The result was a double decomposition of both reagents, and this was limited in both cases. Thus it is proved that the chemical reactions which take place between solid bodies under great pressure obey the same law as the reactions which take place in solutions.

It is thus established that the reciprocal solubility of substances is not only a condition of their agglutination in the solid state, but also of their chemical combination under the influence of pressure. Without doubt this is the only condition necessary with regard to agglutination, but not in so far as it concerns chemical reaction.

(To be continued).

Society of Arts.—In consequence of the Annual Dinner of the Institution of Electrical Engineers being fixed for Monday, December 3rd, the second lecture of Professor Fleming's Cantor course on "Electric Oscillations and Electric Waves," announced for that date, will be postponed until the following day, Tuesday, December 4th, at 8 o'clock, to suit the convenience of members and others who might be prevented by the dinner from attending it.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1900.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, November 9th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oa. 1st to Oa. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, one was returned as "turbid," all the others were clear, bright, and well filtered.

The rainfall at Oxford during October again shows a deficiency, though rain fell on fifteen days out of the month; the actual rainfall was 2.35 inches, the average fall is 2.75 inches; this leaves a deficiency of 0.40 inch for the month and brings the total deficit for the year up to 2.45 inches, or 11.5 per cent on the thirty years' average.

Our bacteriological examinations of 551 samples have given the results recorded in the following table; we have also examined 40 other samples, from special standpipes, &c., making a total of 591 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	184
New River, filtered (mean of 125 samples) ..	10
Thames, unfiltered (mean of 27 samples) ..	1441
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 301 samples) ..	26
Ditto ditto highest	336
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	212
River Lea, from the East London Company's clear-water wells (mean of 44 samples) ..	15

Of the 470 samples of filtered water supplied to London, examined bacteriologically during the past month, thirty samples, or 6 per cent of the whole number of samples examined, contained more than 100 microbes per c.c.

The fact that 6 per cent of the samples collected this month contained more than 100 microbes per c.c., as compared with 2 per cent last month, may be accounted for by the large increase of rainfall over that of the previous month; in September, as will be seen by our last report, only 0.41 inch of rain fell, while during October 2.35 inches have been recorded. At the same time we are able to state that a number of special daily examinations have failed to show the presence of any pathogenic microbes in any sample of filtered water.

It is understood that the moment we discover any sample from the clear-water wells which contains more than 100 microbes per c.c., or shows any trace of turbidity, we at once communicate with the Water Company, and inform

them that certain of their filters are working defectively, and ought to be instantly remedied.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES,
JAMES DEWAR.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 238).

Dilatometer Experiments (continued).

Experiment 24.—The same dilatometer was again heated slowly up to 217° , the following readings being obtained:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
117°	132	2 : 56	160°	225	3 : 24
130	161	3 : 02	172	250	3 : 39
140	182	3 : 14	182	271	3 : 49
150	203	3 : 18	201	311	4 : 15

The tube was then cooled down—

Temp.	Scale.	Time.
169°	248	4 : 27
155	219	4 : 32
120	145	4 : 52

then heated to 225° to effect fusion, after which the following readings were obtained on cooling down:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
225°	415	5 : 37	165°	290	5 : 57
185	336	5 : 41	150	257	6 : 01
—	332	5 : 42	130	212	6 : 12
—	332	5 : 50	69	82	6 : 18
180	322	5 : 52			

This shows that melted selenium in paraffin may be cooled down quite slowly without any transformation taking place, for the last of the above readings agrees with that found for the vitreous form in the preceding experiment where the bulb was cooled at once from 220° to 57° . In order that the paraffin might not solidify, the tube was placed over night in water which varied in temperature from 60° to 75° ; on the following morning, a reading was taken at 74° and the level was found to be 78, showing that the selenium had suffered contraction, but had not gone over entirely to the metallic form. On then raising the temperature, the following readings were made:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
74°	78	10 : 50	111°	127	10 : 30
85	100	11 : 02	111.5°	125	11 : 50
90	108	11 : 05	148	199	12 : 09
95	118	11 : 09	200	309	12 : 33
105	132	11 : 19	152	205	12 : 49
109	131	11 : 26			

These observations were made in diffused daylight. The experiment still further confirms the statement that metallic selenium undergoes no change in being heated to 200° , and that when the temperature is brought back to 150° the reading accords with that obtained with rising temperature.

The indications of a partial change at about 70° , followed by no further contraction up to 105° , are of interest, and a further experiment was undertaken later on in the hope of being able to repeat these observations. The following is the experiment in question:—

Experiment 71.—Selenium in solid paraffin. During three hours the temperature was slowly raised from 55° to 97° without any indication of a change; at this point contraction began; but the apparatus being left to itself, the temperature gradually fell during the succeeding four hours, to 73° ; the change had then proceeded to a con-

siderable extent; further heating at higher temperatures brought out the fact that below 90° the change, even when it has commenced, goes on very slowly—at 80° it amounted to about three scale divisions in an hour, where the total contraction involved nearly 80 scale divisions—but the drop was continuous and reached a limit after about fourteen hours' heating at temperatures between 80° and 90° . This experiment comes in a later class than the preceding, and was made with a weighed quantity of selenium and a dilatometer whose capillary arm had been previously calibrated. This method of procedure is much to be recommended for cases like the present, since it makes it possible to estimate at any moment approximately the density of the material studied.

The final density of the selenium was found in this way to be 4.83. The extreme slowness with which the change goes on at 80° suggests that the observations of Experiment 24 may have no special significance at all; the change was probably incomplete and did not proceed rapidly to an end until the temperature was raised above 100° .

On the other hand, the existence of red crystalline forms of selenium, which, according to Muthmann, go over to metallic selenium at 110 – 120° , and which have a density of about 4.5, points to the possibility of the occurrence here, exceptionally, of such a form; in that case Experiment 71 simply failed to reproduce the red form. It should be said, further, that no indication whatever of a change of vitreous selenium into the red crystalline modification was observed in any of the other dilatometer experiments, although such a change is known to go on superficially when vitreous selenium is brought into carbon disulphide at ordinary temperatures.

The following experiments were made with liquid paraffin unless otherwise stated:—

Experiment 26.—This determination was made as a further study of the density relations of the form of selenium which is produced when the melted element is cooled to 200° and maintained at that temperature until no further change of volume is observed. A dilatometer containing vitreous selenium was placed in a bath at about 150° ; at this temperature the change is immediate and gives rise, as is well known, to the ordinary metallic selenium. The experimental data are as follows:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
155°	260	12 : 12	219°	531	12 : 47
160	273	12 : 14	200	478	12 : 54
178	323	12 : 20	—	468	12 : 56
198	380	12 : 25	202	461	1 : 06
210	413	12 : 30	200	450	1 : 11
218	440	12 : 33	—	444	1 : 13
220	460	12 : 35	—	438	1 : 15
221	530	12 : 43			

At this point the temperature was allowed to drop for a few moments to 182° ; it was raised again at once:—

Temp.	Scale.	Time.
185°	370	1 : 25
198	386	1 : 31
201	393	1 : 32
196	380	2 : 06

The material was then heated again to fusion, and cooled to 200° :—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
201°	500	3 : 10	200°	443	3 : 49
199	490	3 : 11	200.5°	430	3 : 56
198	485	3 : 13	—	418	4 : 11
199	485	3 : 17	198	398	4 : 17
—	485	3 : 20	—	395	4 : 24
200	479	3 : 28	197	389	4 : 44
—	469	3 : 35	199	393	4 : 54
—	461	3 : 39			

This experiment shows clearly that the form produced at 200° is identical with the original metallic selenium. The slight difference in the readings at 200° before and after fusion, is negligible in comparison with the total

* From the *Journal of Physical Chemistry*, vol. iv.,

change of level involved in the transformation. The heating at 220° to effect fusion was prolonged until there was little or no further change during several minutes, since it was plainly desirable to have the mass of selenium free from crystals of the metallic form; on the other hand, there was no object in refining too far upon this point, since we may say certainly that in the cooling down from 220° to 200° there would always be a small quantity of material deposited from the solution, either in the form of metallic crystals, or perhaps in some other modification if such were capable of existence at that temperature.

Experiment 28.—This experiment, which was made with the dilatometer used in Experiment 27, was undertaken to determine whether or not there are two substances in the melt when selenium is brought to complete fusion and then allowed to go over partially at 200°. If two forms are present in the liquid state, forming but one phase, then the melting-point will be lowered, and in consequence, at temperatures below—but very near—217°, any of the solid form present will melt and the dilatometer level will rise; if such is not the case it will continue to fall. The readings were as follows:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
80°	44	9 : 47	221°	558	12 : 01
100	92	9 : 54	200	497	12 : 06
190	350	10 : 32	201	469	12 : 39
207	398	10 : 50	199.5	447	12 : 48
218	433	11 : 02	214	483	12 : 54
220	530	11 : 29	215	478	1 : 08
—	553	11 : 53	214.5	474	1 : 15

It is plain from these figures that at 215°, under the conditions of the experiment, the contraction continued. The recorded temperatures are uncorrected; on comparing the thermometer used with a standard thermometer calibrated at the Reichsanstalt in Berlin, it was found that the one used in these experiments registered 3° too low at 215°. Since selenium expands on melting, it follows from the theorem of Le Chatelier that the melting-point will be raised by increased pressure; but as the prevailing pressure within the tube was, in this experiment, not above 6 to 8 atmospheres, it is improbable that this would very sensibly affect the melting-point. Reicher (*Recueil Trav. Pays-Bas*, 1884, ii., 262) found that an increase of 4 atmospheres only raised the inversion point for rhombic and monoclinic sulphur by about 0.2°, whereas the melting-points of various substances—water, naphthalene, &c.—are even less sensitive to pressure changes (Ostwald, "Lehrb.", i., 1013). It seems most likely in this case that the recorded value 217° is somewhat low and that the melting-point of grey selenium should be placed nearer 220°. At any rate the experiment shows that liquid selenium continues to go over into the solid form at temperatures lying very near the melting-point, and this renders the existence of a second form in the liquid phase most improbable.

Experiment 29.—This determination was conducted with the same dilatometer that was used in Experiment 28. Starting from vitreous selenium, the following readings were made:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
55°	60	2 : 38	191°	418	2 : 49½
80	125	2 : 41	197	419	2 : 50
132	270	2 : 45	202	407	2 : 54
158	350	2 : 47	204	406	3 : 06
172	385	2 : 48	201	396	3 : 57
185	410	2 : 49	195	380	5 : 20

This experiment shows that it is sometimes possible, by rapidly raising the temperature of vitreous selenium, to heat it to about 185° before the transformation begins; but a comparison with the readings in Experiment 26 shows that the form produced in this way at 200° is the same as that obtained by any of the other methods used; and, furthermore, its density is not changed by heating for two and one-half hours at about 200°.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 1st, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

MESSRS. S. S. Napper, G. E. Tomlins, O. Silberrad, C. Watson, C. T. F. Watts, and H. F. F. B. Fernor were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Messrs. George Lowe Bennett, 13, St. Domingo Vale, Egerton, Liverpool; Frederick Nisbett Binks, 2, Holywell Terrace, Millbourne Avenue, Drumcondra, Dublin; Herbert James Singleton Boyes, 9, Rua Episcopal, Sao Paulo, Brazil; Theodore Ridley Burnett, 83, Coltart Road, Liverpool; John Henry Cheesewright, 80, Sydney Road, Hornsey, N.; Albert Walker Comber, Rio Marina, I. d'Elba, Italy; Alexander Davidson, jun., 1, Almond Bank Terrace, North Murchiston, Edinburgh; Arthur Louis William Fechtner, 186, Spring Bank, Hull; Willie Ludford Freeman, 102, Marlboro' Road, Oxford; William Gasson, Kimberley, South Africa; George William Gibbings, Standard Bank of South Africa, Ltd., Salisbury, Mashonaland; John Gibson, Battle Hill, Hexham, Northumberland; Walter Augustus Handcock, Southbank, 40, Avenue Road, Highgate, London; William Arthur Hargreaves, Port Adelaide, South Australia; George Harker, 35, Boulevard, Petersham, Sydney, N.S.W.; Frank C. R. Hemingway, Albans, Forest Road, Walthamstow; John Brownlie Henderson, Brisbane, Queensland; Samuel Hewitt, 3, Chester Street, Norwich; William Henry Hewitt, 115, Fentiman Road London, S.W.; Adolf Jappé, Broad Oak, Oak Avenue, Bradford; Humphrey Owen Jones, Clare College, Cambridge; George Washington Kilner, 14, St. John's Park, Upper Holloway, N.; Morris Charles Lamb, Herold's Institute, Drummond Road, Bermondsey, London, S.E.; George Druce Lander, 1, Balmoral Road Nottingham; William McCall, Rio Marina, Isola d'Elba, Italy; Thomas Marginson Nightingale, 375, Bridgman Street, Bolton; Alexander Pardy, Pietermaritzburg, Natal, S. Africa; John Paul, Bacteriological Institute, Grahamstown, Cape Colony; Ernest Vivian Pearce, The Beaches, Hayle, Cornwall; Henry Ernest Stapleton, St. John's College Oxford; Arthur Lambert Thornton, 2, Park Street, Bolton; Ferdinand Gerhard Wiechmann, 771, West End Avenue, New York; George Sampson Valentine Willis, Southwood, Croham Road, South Croydon; Walter Bourne Woodbridge, Grey Friars, Chichester; Herbert Edwards Wright, 1, Brewers Street, St. Aldates, Oxford.

Of the following papers those marked * were read.

* 132. "Action of Alkalis on Nitro-compounds of the Paraffin Series. Part II. The Reactions and Constitutions of Methazonic Acid and the Formation of Isoxazoles." By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING, B.Sc.

In a previous paper (Dunstan and Dymond, *Trans.*, 1891, lix., 410) it was shown that trimethyl isoxazole results from the action of alkalis on nitroethane, and triethylisoxazole from a similar action on nitropropane. Nitromethane, however, furnished no isoxazole, neither did secondary nitropropane.

Further investigation has shown that the action of alkalis, preferably ammonia, on nitromethane leads to the production of the substance briefly described by Lecco under the name of *methazonic acid*, $C_2H_4N_2O_3$, and regarded by him as an anhydride of nitromethane. The authors have obtained this substance in colourless crystalline plates melting between 60° and 70°, and have prepared and described several of its salts. Both the acid and its salts, $AgC_2H_3N_2O_3$, $NH_4C_2H_3N_2O_3$, &c., are unstable, and are liable to explode when suddenly heated.

When heated with acids or alkalis, methazonic acid breaks up into carbon dioxide, hydrogen cyanide, and hydroxylamine, according to the equation—

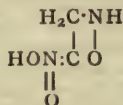


It is proved that 1 atom of nitrogen appears as hydrogen cyanide, and the other as hydroxylamine, whilst the carbon is equally divided between the carbon dioxide and the hydrogen cyanide.

On oxidation with permanganate, chromic acid, or hydrogen peroxide, methazonic acid furnishes carbon dioxide, hydrogen cyanide, and nitric acid. On reduction, either in acid or alkaline solution, with weak or strong reducing agents, the principal products are ammonia and formic acid. No trace of ethylene-diamine or methylamine could be found.

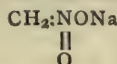
Alkyl derivatives of methazonic acid can be prepared, but they are highly unstable.

The authors propose the formula—

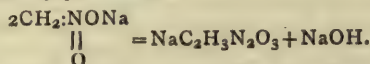


for methazonic acid as satisfactorily accounting for its reactions.

Adopting the view of Nef that the "salts" of the nitroparaffins are to be regarded as derived from a tautomeride, and writing the formula of sodium nitromethane as



the authors show how methazonic acid is formed by a process of intermolecular oxidation followed by condensation of the nitromethane residue with formaldoxime simultaneously produced,—



By a similar process of intermolecular oxidation, followed by condensation with an oxime, it is shown how trimethylisoxazole, acetonitrile, and sodium nitrite are formed by the action of alkalis on nitroethane and how triethylisoxazole and similar products result from the action of alkalis on primary nitropropane; also, how secondary nitropropane gives no isoxazole, but acetone, nitrite, and hydroxylamine.

In this discussion it is assumed that nitro-compounds may be reduced to oximes (Dunstan and Dymond, *Proc.*, 1894, 139), and grounds are now stated for concluding that whilst the nitroparaffins themselves may be reduced (in acid solution) to substituted hydroxylamines, their salts, when reduced (in alkaline solution), furnish oximes or their decomposition products. These facts afford further justification for the view that the "salts" of the nitroparaffins are derivatives of a tautomeride containing the group—

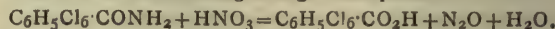


*133. "*Hexachlorides of Benzonitrile, Benzamide, and Benzoic Acid.*" By FRANCIS EDWARD MATTHEWS.

Benzonitrile mixed with water is saturated with chlorine and exposed to light till the yellow colour of the chlorine disappears. This process is repeated four or five times. The mixture is then subjected to steam distillation till all the benzonitrile has passed over. A thick oil remains, which, on purification by solution in and subsequent recrystallisation from glacial acetic acid, gives colourless crystals of benzonitrile hexachloride, $\text{C}_6\text{H}_5\text{C}_6\text{Cl}_6\text{CN}$, melting at 157° .

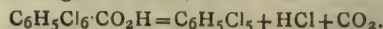
The hexachloride is not easily hydrolysed, but heating with strong sulphuric acid at 170 — 180° converts it into the hexachloride of benzamide,

This, crystallised from acetic acid, melts at 187 — 188° . On treating the hexachloride of benzamide with fuming nitric acid, the following change takes place:—



The hexachloride of benzoic acid has been obtained pure, and has been analysed.

Its most striking property is the decomposition it undergoes on boiling with water, thus:—



The benzoic acid hexachloride and the monochlorobenzene tetrachloride are being further investigated.

*134. "*The Influence of Solvents on the Rotation of Optically Active Compounds.*" I. By T. S. PATTERSON.

Experiments to determine the influence of some solvents on the rotation of ethyl tartrate at various concentrations and temperatures were described. From the data obtained it is possible to deduce the rotation in each of the solvents dealt with, at any temperature within the limits of the experiments and at any concentration whatever, with fair accuracy.

The results obtained may be summarised thus;—

1. *Water.*—Ethyl tartrate in dilute aqueous solution has a much higher specific rotation than in the pure state. In solutions weaker than 55 per cent the rotation diminishes with increase of temperature.

2. *Methyl Alcohol.*—In dilute solution in methyl alcohol the specific rotation of ethyl tartrate is considerably higher than in the pure state.

In all solutions the specific rotation increases with increase of temperature, and at much the same rate as that of the pure ester.

3. *Ethyl Alcohol.*—Dilute solutions of ethyl tartrate in ethyl alcohol have a specific rotation slightly higher than that of the pure ester.

A maximum value of the specific rotation only seems to be reached at infinite dilution.

Increase of temperature causes increase of rotation in all solutions, the rate of variation being much the same as in the pure ester.

4. *Propyl Alcohol.*—No mixture of ethyl tartrate and propyl alcohol seems to have a higher specific rotation than pure ethyl tartrate at temperatures below 30° . At higher temperatures this is not the case.

The specific rotation in all solutions increases with increase of temperature, the rate of increase being generally slightly greater than in the pure ester.

5. *Glycerine.*—Dilute solutions of ethyl tartrate in glycerine have a considerable higher specific rotation at low temperatures than the pure ester, but as in the case of ethyl alcohol, the maximum rotation appears to be reached only at infinite dilution.

The influence of increase of temperature is in all cases to increase the rotation, the rate of increase being in dilute solutions less and in concentrated solutions greater than for the pure ester.

The data obtained were then discussed in order to trace, if possible, the variation in rotation of the dissolved ethyl tartrate to some known property of the solvent. It was suggested that the property known as internal pressure possesses the necessary qualifications, and investigation seem to justify its choice. Since the data obtained render the calculation of molecular solution volume possible, this was first compared with the rotation, and it was shown that a regularity can be established, and that the variation of rotation with change of temperature may be explained by certain assumptions regarding the variation of the asymmetry of a molecule with the variation of its volume.

These phenomena of rotation were then traced back a step further to internal pressure, or what is probably the same thing—heat of disgregation, when very similar regularities are observed, which seems to show that the original assumptions, regarding the dependence of solution volume on internal pressure and of rotation on both, are justified.

*135. "The Action of Heat on Ethyl Sulphuric Acid." By WILLIAM RAMSAY and G. RUDORF.

Ethyl hydrogen sulphate, when heated, yields as gaseous products of decomposition, sulphur dioxide, carbon dioxide and monoxide, and ethylene. The oxides of carbon, after the reaction has fairly started, are present in approximately equivalent proportions; this seems to point to the oxidation of the alcohol to oxalic acid, which is at once decomposed by the sulphuric acid. But glycol, heated with sulphuric acid, yields no carbon monoxide, hence this explanation is of questionable validity. When ethylene is bubbled through hot sulphuric acid, the products are the same in kind, and approximately the same in relative amount, as when hydrogen ethyl sulphate is heated. It was proved, in conclusion, that even at 250° carbon monoxide does not deprive sulphuric acid of oxygen; hence the formation of carbon dioxide in the preceding experiments cannot be attributed to the oxidation of carbon monoxide; it must have been a direct product of the reaction.

*136 "Contributions to the Knowledge of Fluorescent Substances. I. The Nitro-derivatives of Fluorescein." By J. T. HEWITT and B. W. PERKINS.

Attention has been called to the non-fluorescence of the alkaline salts of tetranitrofluorescein (R. Meyer, *Zeit. Phys. Chem.*, 1897, xxiv., 468; and Hewitt, *Proc.*, 1900, xvi., 3; and *Zeit. Phys. Chem.*, 1900, xxxiv., 1). This absence of fluorescence might possibly be explained by the existence of such tautomerism between the hydroxyl and nitro-groups as usually occurs with ortho- and para-nitrophenols, which would inhibit the double symmetrical tautomerism which, as one of the authors has previously pointed out, is so characteristic of many fluorescent substances. Under these circumstances it seemed very desirable to subject dinitrofluorescein to a further study, since this substance has only been analysed as a hydrate, $C_{20}H_{12}(NO_2)_2O_6$ (von Baeyer, *Annalen*, 1876, clxxxiii., 32). In order to obtain the true anhydrous dinitrofluorescein, its diacetyl derivative, which may be prepared by the action of acetic anhydride on the hydrate, was hydrolysed with fairly concentrated sulphuric acid (80 per cent). The anhydrous compound thus obtained dissolves in cold dilute soda solution with an orange-brown colour and with no trace of fluorescence. On warming, the solution readily goes blue, a salt of the hydrate being produced.

To determine the position of the nitro-groups in dinitrofluorescein, potash fusion was resorted to, and a small quantity of a substance of m. p. 114° (uncorr.) obtained. Nitrosorcinol (OH : OH : NO₂ = 1 : 3 : 4) melts at 115°.

Tetranitrofluorescein has also been examined, but the authors have been unable to obtain von Baeyer's numbers on analysis, the results always pointing to the formula $C_{20}H_{10}(NO_2)_4O_6$. Hence arguments deduced from the non-fluorescence of alkaline salts of this compound have no bearing on the question as to whether a pyrone ring is a "fluorophor" as the pyrone ring does not exist in the compound. Hence the results obtained with regard to the non-fluorescence of the alkaline solutions of dinitrofluorescein are especially significant, since in this compound the pyrone ring may be preserved intact and the fluorescence inhibited by the nitro-groups alone.

137. "Derivatives of Ethyl α -Methyl- β -phenylcyanoglutarate." By W. CARTER and W. TREVOR LAWRENCE.

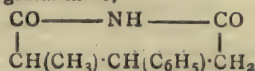
When ethyl cinnamate and ethyl sodiocyanacetate are allowed to interact in alcoholic solution, methyl iodide being subsequently added to the condensation product, it is found that the neutral reaction mixture consists almost entirely of equal quantities of the two stereoisomeric forms of ethyl α -methyl- β -phenyl- α -cyanoglutarate, $C(CO_2Et)(CH_3)(CN) \cdot CH(C_6H_5) \cdot CH_2(CO_2Et)$.

The α -modification is a crystalline solid, crystallising from ligroin in prisms which melt at 89°, the β -modification is a liquid boiling at 260° (100 m.m.); both isomerides, on addition of alcoholic potash, are converted into micro-

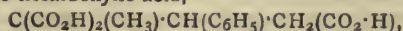
crystalline potassium salts, which separate completely from the mother-liquor.

From these potassium salts two distinct acids are obtained. The α -acid is fairly soluble in water, from which it separates slowly in prisms, melting with decomposition at 161°; the β -acid is much less soluble in water and melts at 194°.

Both acids are converted by hydrochloric acid into methyl-phenyl-glutarimide,—



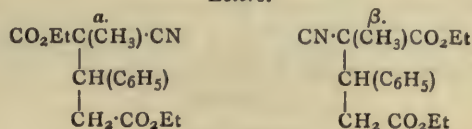
(prisms from water, m. p. 144°), and are completely hydrolysed by sulphuric acid with formation of methyl-phenyl-glutaric acid; on prolonged boiling with aqueous potash, they are converted into α -methyl- β -phenyl- α - γ -propane-tricarboxylic acid,—



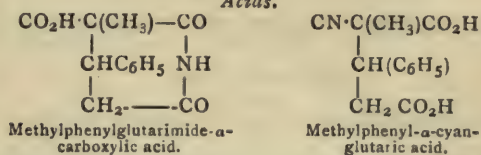
which crystallises from a mixture of chloroform and acetone, and melts, with decomposition, at 148°.

Acetyl chloride offers a means of differentiating between the two modifications, as it converts the α -acid into a substance melting at 110°, which possesses acid properties, and is easily decomposed by water, whereas the β acid forms a neutral substance melting at 146°, which is fairly stable towards water. The following formulæ have been assigned to the α - and β -esters, acids, and acetyl derivatives:—

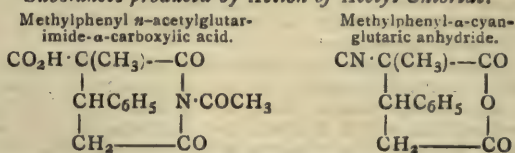
Esters.



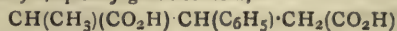
Acids.



Substances produced by Action of Acetyl Chloride.



By this reaction methylphenylglutaric acid, previously obtained with great difficulty (Avery and Fossler, *Amer. Chem. Journ.*, 1899, xx., 516), may be easily prepared. α -Methyl- β -phenylglutaric acid,—



crystallises from water or ligroin in prisms (m. p. 125°); theoretically, the acid should exist in two modifications, but up to the present time the authors have only isolated one form, which from its easy conversion into the anhydride, is probably the *cis*-modification.

Acetyl chloride converts the acid into a double anhydride with acetic acid, which crystallises from benzene in asbestos-like masses, melting at 107°; its formula is $[\text{C}(\text{CO} \cdot \text{O} \cdot \text{COCH}_3)\text{H}(\text{CH}_3)\text{CHC}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CO}]_2\text{O}$. When this is distilled, the true anhydride of methylphenylglutaric acid is obtained as a gum which slowly solidifies to a solid mass melting at 74°; the corresponding anilic acid is also a gum.

Methylphenylglutaric acid is unacted upon by boiling permanganate solution; boiling with fuming nitric acid converts it into two nitro-derivatives, of which the less soluble melts at 208° and the more soluble at 179°; both

substances possess the formula $C_{12}H_{13}O_4NO_2$, and are probably *o*- and *p*-nitrophenylmethylglutaric acid.

138. "The Nitration of Acetamino-orthophenyl Acetate (Diacetylorthoaminophenol)." A correction. By RAPHAEL MELDOLA, F.R.S., and ELKAN WECHSLER.

The object of this note is to correct and extend the statement (Meldola, Woolcott, and Wray, *Trans.*, 1896, lxi., 1325) that the nitration of acetamino-orthophenol acetate under the conditions specified gave a mononitro-derivative, which, on further nitration, gave a dinitro-derivative. A repetition of this work has led to the conclusion that a dinitro-derivative is produced under all conditions of nitration. The statement in the paper above referred to was based on an error of analysis. The dinitro-derivative crystallises from hot water in long, ochreous needles melting at 201° , and softening at a temperature some degrees lower.

Two experiments gave $N=17.30$ and 17.39 per cent respectively. $C_6H_5(NO_2)_2NHAc \cdot OH$ requires $N=17.42$ per cent.

One acetyl group is split off during nitration. The dinitro-derivative is readily hydrolysed by boiling for a short time with sodium hydroxide solution, and the dinitroaminophenol thus obtained proved to be *picramic acid* as shown by the melting point ($167-168^\circ$), by conversion, by the diaza-method, into 2-chloro-4:6-dinitrophenol of m. p. $110-111^\circ$, and by a comparison of the properties of the diazoxide with the description of this compound given by Griess (*Annalen*, cxiii. 205).

The nitration of diacetyl orthoaminophenol thus gives rise to the direct formation of 2-acetamine-4:6-dinitrophenol, and the formulæ given in that section of the the previous paper must be revised accordingly.

(To be continued).

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

October 16th, 1900.

Prof. HORACE LAMB, F.R.S., President, in the Chair.

PROF. H. B. DIXON, F.R.S., communicated a summary of the results of experiments, conducted in conjunction with Mr. F. W. Rixon, B.Sc., on the "Specific Heat of Gases at High Temperatures."

As part of a larger investigation, the authors have determined directly the specific heat of carbonic acid, up to $400^\circ C.$, at constant volume. The gas is screwed up in a mild steel cylinder, which is heated in a gas oven running on rails. The oven and cylinder can thus be brought quickly over the calorimeter, into which the cylinder falls through trap doors forming the bottom of the oven. The transference is thus effected with a minimum loss of heat. The difficulties arising from splashing and from escape of steam are overcome by dropping the cylinder into a glass tube dipping some distance below the water. The glass tube breaks at a crack made in the neck, and thus ensures a complete immersion of the hot cylinder at a good depth in the water, which closes over the cylinder in a cataraet.

A similar experiment being performed with the empty cylinder, the difference gives the heating effect of the gas.

The results given below for CO_2 show that the method, which it is hoped may still be improved, is a workable one.

Initial temp. of gas.	Final temp.	Mean.	Spec. heat.
115	16	65.5	0.200
192	16	104	0.211
298	21	159.5	0.288
398	21	209.5	0.356

The authors are now measuring the specific heat of nitrogen in the same way.

NOTICES OF BOOKS.

Flesh Foods, with Methods for their Chemical, Microscopical, and Bacteriological Examination. By C. AINSWORTH MITCHELL, B.A. (Oxon.), F.I.C., F.C.S. With Illustrations and a Coloured Plate. London: Charles Griffin and Co., Ltd. 1900. Pp. 336.

THE author has herein collected and summarised in a convenient form, records of investigations which are for the most part scattered throughout English and foreign scientific books and periodicals, and has selected those methods which appeared to be most suitable for the examination of meat and its preparations. The book forms an excellent practical handbook for medical men, analysts, inspectors, and others who may be called upon to judge the quality of various samples of flesh foods and derivatives.

The value of flesh as a food, apart from the nature of the animal it is taken from, is largely based on its colour, consistency, &c., on the proportion of fat, and on its taste and smell. It is not, however, possible to detect diseased meat with any certainty by chemical means, and it requires a good deal of practice to form a correct judgment from its appearance; still, there are certain tests, and they are fully described here.

The manufacture of meat extracts is a branch of trade which has increased enormously of late years; it is, however a great, though common mistake, to think that these widely advertised products are of much, if any value as food; Liebig expressly stated that his extract of meat was to be regarded as a stimulant, like tea or coffee, and not as a food, and his view is in the main confirmed by the experiments of later chemists; C. Voit, for instance, asserts that extract of meat is practically useless as food. In some products, eight or ten per cent of meat fibre is added with a view to giving them some food value, but it is obvious that a large quantity would have to be absorbed to get even as much nourishment as there is in an egg.

By means of bacterial examination it is often possible to supplement the information to be obtained from the chemical and microscopical examination of flesh. All the various forms of bacteria, known as *bacilli*, *micrococci*, and *spirilla*, may be found in sound or diseased meat, and in the chapter on this subject the author fully describes the more important ones. Sausages appear to be particularly deadly, some fresh uncooked ones have been found to contain over 6,000,000 microbes per grm. of meat, and as many as 9000 per grm. after being boiled for thirty minutes.

On the other hand, it is cheering to read that, according to Herdmann and Boyce, the typhoid bacillus does not increase in the tissues of the oyster, but perishes in its intestines; sea water also appears to be inimical to its development. Taking shell-fish in general, the *Bacillus coli communis* was sometimes found by these observers in those sold in towns, but there was no evidence as to its occurrence in molluscs taken from pure water. In no instances were any organisms giving all the reactions of *B. typhosus* isolated, though some of the bacilli resembled them in certain characteristics.

The book is well written and contains a fund of valuable and interesting information, and is provided with a very complete index of forty-eight columns.

Industrial Chemistry in Germany. ("L'industrie Chimique en Allemagne"). Its Economic, Scientific, and Commercial Organisation. By A. TRILLAT. In One Volume, Illustrated. Paris: J. B. Baillière and Sons. 1900. Pp. 500.

THE principal points dealt with by the author are the commercial prosperity of Germany, which he attributes to technical education and commercial organisation, the action of the German Chambers of Commerce, their patent laws, &c.

The first part of the book deals with the general situation in Germany; in the second part, which is of the greatest interest, the author describes the great chemical industries, such as metallurgy, soda processes, the manufacture of acids and alkalis, chemical products and drugs, organic and mineral colouring matters and allied subjects, artificial manures, ammoniacal salts, explosives, sugar making, porcelain and glass-working, electro-chemical and electro-metallurgical processes, &c.

The third, fourth, and fifth parts take in detail the economic and scientific organisation of chemical industry, and include an examination of the causes which have contributed to the progress of these arts in Germany.

A perusal of this book will be of interest both to practical men and to those who have to do with the organisation of laboratories and teaching institutions, and many useful hints will be gained therefrom.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 18, October 29, 1900.

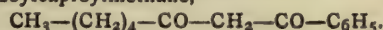
Ammoniacal Arsenates of Nickel.—O. Ducru.—The author's researches establish the existence of four arsenates of nickel:— $(\text{AsO}_4)_2\text{Ni}_3 + 1.5\text{H}_2\text{O}$, $(\text{AsO}_4)_2\text{Ni}_3 + \frac{2}{3}\text{NH}_3 + \text{H}_2\text{O}$, $(\text{AsO}_4)_2\text{Ni}_3 + \frac{2}{3}\text{NH}_3 + \frac{1}{2}\text{H}_2\text{O}$, and $(\text{AsO}_4)_2\text{Ni}_3 + \frac{2}{3}\text{NH}_3 + \frac{1}{3}\text{H}_2\text{O}$. These latter three ammoniacal arsenates of nickel correspond to those of cobalt, and are derived from annabergite by the replacing of H_2O by NH_3 , molecule by molecule. To prepare these ammoniacal arsenates of nickel and cobalt, it is necessary to use solutions in which the amount of free ammonia has been determined. The reaction takes place in sealed tubes. Under these conditions only small quantities of the products are obtained. The author therefore found it advisable to use specially constructed hermetically sealed flasks, in which 400 to 500 c.c. can be heated at once. The whole was placed on an air-bath at 155°C , and surrounded by metal-foil.

The Selenides of Cobalt.—M. Fonze-Diacon.—By the action of selenium vapours on red-hot cobalt, Little obtained the protoselenide, CoSe , in an amorphous condition. The author prepares a series of cobalt selenides analogous to those of nickel, according to the conditions under which the reaction takes place. These are respectively CoSe_2 , Co_2Se_3 , Co_3Se_4 , CoSe . At a high temperature, hydrogen transforms these substances into a sub-selenide, Co_2Se , which, when left to itself, gradually loses its selenium. Cobalt selenate, when reduced by hydrogen, gives a series of oxyselenides or mixtures of selenide and metallic cobalt, according to the temperature at which the reduction takes place.

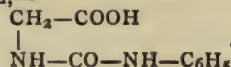
Modification of the Chemical Properties of some Simple Bodies by the Addition of very small Quantities of Foreign Materials.—Gustave Le Bon.—During researches on the various forms of phosphorescence, the author discovered that when minute quantities of foreign matter were added to certain substances, a combination was formed which profoundly modified the physical properties of these bodies. These changes in the physical state of various substances led to the question as to whether the chemical properties of certain bodies were equally modified by the presence of traces of foreign matter. The author's researches were made upon mercury, magnesium, and aluminium. In all cases a decided modification was observed when minute traces of mercury were added to magnesium or aluminium.

Cellulose, Mercerised Cellulose, Precipitated Cellulose, Hydrocellulose.—Léo Vignon.—Cellulose and some of its modifications form the base of natural vegetable textiles and of artificial textiles whose substance is of vegetable origin. The author examined comparatively, from a chemical point of view, cotton cellulose, mercerised cellulose, cellulose dissolved in Schweitzer's reagent, and precipitated by acids, and Girard's hydrocellulose, with regard to their reducing properties, velocity of saccharification, and heats of combustion. He concludes from the numbers obtained that concentrated alkalis, such as are used in the operation of mercerising and probably hydrating, depolymerise the cellulose, without conferring on it new chemical functions. The same thing is true of dilute acids acting under the conditions necessary for the formation of Girard's hydrocellulose.

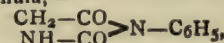
Two Acetones of the Acetylenic Series. Acetylcenanthylidene and Benzoylcenanthylidene. Transformation into β -dicetones by Hydration.—Ch. Moureu and R. Delange.—The action of acetyl chloride and benzoyl chloride on sodium cenanthylidene gives two acetylenic acetones. Acetylcenanthylidene, $\text{CH}_3-(\text{CH}_2)_4-\text{C}\equiv\text{C}-\text{CO}-\text{CH}_3$, and benzoylcenanthylidene, $\text{CH}_3-(\text{CH}_2)_4-\text{C}\equiv\text{C}-\text{CO}-\text{C}_6\text{H}_5$. These two new compounds, under the influence of sulphuric acid, fix a molecule of water, giving two new β -dicetones: acetylcaprolymethane, $\text{CH}_3-(\text{CH}_2)_4-\text{CO}-\text{CH}_2-\text{CO}-\text{CH}_3$, and benzoylcaprolymethane,—



Transformation of α -Amide Acids into Phenylhydantoins.—A. Mouneyrat.— α -Amide acids combine in alkaline solution with phenyl isocyanate, giving acid phenylureides; with glycolol, for example, acetic phenylureid is obtained,—



Phenylhydantoin, prepared by means of glycolol, corresponds to the formula,—



and is identical with the substance which Guareschi prepared by combining glycine with phenylurea. The author obtains analogous substances with alanine, α -aminobutyric acid, leucine, and phenylalanine.

Gaseous Exchange between the Atmosphere and Entire Plants.—Th. Schloesing, junr.—The author's experiments were conducted on plants when their only source of nitrogen was from ammoniacal salts. He finds that plants are capable of using ammoniacal nitrogen in almost the same way as nitrogen of nitric origin. As in all preceding experiments, he finds that entire plants evolve more oxygen than that due to the carbon dioxide they decompose; this being due to the reduction of mineral salts drawn from the soil.

Researches on the Cystine in Contaminated Waters.—M. Molinier.—The author's researches lead him to the conclusion that all waters having an acid reaction, even distilled water, when submitted to Causse's reagent, give an orange colouration, not destroyed by sulphuric acid.

MISCELLANEOUS.

Messrs. Perkin, Son, and Co., Limited, have just issued a new Catalogue of photographic apparatus, magic lanterns, and accessories, among which may be specially mentioned their "Optimus" lenses of various kinds, such as "europsopes," wide angle and portrait lenses, cinematographs, &c. Attention is also drawn to the "Ubique" hand camera, and the "Optimus" portable sets of photographic apparatus, which may be depended on for giving good results.

Action of Sulphurous Anhydride on the Metallic Sulphates, and especially on Ferric Sulphate.—U. Antony and E. Manasse.—In the same way as sulphurous acid reacts on sulphate of ruthenium giving a dithionate, so does it act on ferric sulphate. This salt in a 2 per cent solution, that is to say, at the limit of concentration where hydrolysis commences, absorbs SO_2 in the cold. The excess of gas is driven off by a current of CO_2 , and the whole of the SO_4H_2 precipitated from the solution by hydrate of barium, and the excess of barium by exactly the right quantity of CO_2 . The filtered solution contains dithionate of barium; if we treat it with KMnO_4 until the colour remains when hot, then with HCl to decolourise it, we get a precipitate of sulphate of barium, and on filtering it is easily seen that the solution still contains free H_2SO_4 ; this proves the presence of the dithionate in the liquid. The concentration of the ferric solutions, and pressure, have very little influence on the return; on the other hand, temperature has a considerable influence; at 0° we obtain about 80 per cent, falling to nothing at all at 95° .—*Gazz. Chim. Ital.* (1), xxxix, p. 483.

MEETINGS FOR THE WEEK.

MONDAY, 26th.—Society of Arts, 8. (Cantor Lectures). "Electric Oscillations and Electric Waves," by Prof. John A. Fleming, M.A., D.Sc., F.R.S.
WEDNESDAY, 28th.—Society of Arts, 8. "Malaria and Mosquitoes," by Major Ronald Ross.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2140.

ARGON AND ITS COMPANIONS.*

By WILLIAM RAMSAY, F.R.S.,
and
MORRIS W. TRAVERS, D.Sc.

THE discovery of krypton and neon was announced to the Royal Society in the early summer of 1898; and, subsequently, atmospheric air was found to contain a heavier gas to which the name of xenon was applied. Mr. Baly, in the autumn of the same year, called attention to the presence of helium lines in the spectrum of neon, an observation which confirms that made by Professor Kayser, of Bonn, and by Dr. Friedländer, of Berlin.

At the same time we imagined that we had obtained a gas with a spectrum differing from that of argon, and yet of approximately the same density: to this gas we gave the name metargon. It has now been found that the presence of the so-called metargon is to be accounted for by the fact that in removing oxygen from the mixture of these gases, which was then in our hands, phosphorus containing carbon was employed; this mixture when burned in oxygen yields a spectrum to some extent identical with that furnished by carbon monoxide, but differing from it inasmuch as lines of cyanogen are also present. We have no doubt that the so-called metargon, the spectrum of which is visible only at high pressure, and only when impure phosphorus has been employed to remove oxygen, must be attributed to some carbon compound. In spite of numerous experiments we have not yet succeeded in producing any gas in quantity which yields this composite spectrum. It is only to be obtained by a mixture of carbon monoxide with cyanogen.

To obtain the heavier gases krypton and xenon, a large amount of air was allowed to evaporate quietly; the residue was freed from oxygen and nitrogen, and then consisted of a mixture of krypton, xenon, and argon, the last forming by far the largest portion of the gas; this mixture was liquefied by causing it to flow into a bulb immersed in liquid air, and the bulk of the argon was removed as soon as the temperature rose, the krypton and the xenon being left behind. By many repetitions of this process we were finally successful in separating these three gases from each other. While krypton has a considerable vapour-pressure at the temperature of boiling air, the vapour-pressure of xenon is hardly appreciable, and this afforded a means of finally separating these two gases from one another; in the complete paper the operations necessary to separate them are fully described.

For neon the process of preparation was different. The air liquefier furnished a supply of liquid air; the gas escaping from the liquefier consisted largely of nitrogen; this mixture was liquefied in a bulb immersed in the liquid air which the machine was making. When the bulb had been filled with liquid nitrogen a current of air was

blown through the liquid until some of the gas had evaporated. That gas was collected separately, and deprived of oxygen by passage over red-hot copper; it contained the main portion of the neon and the helium present in the air. The remainder of the nitrogen was added to the liquid air used for cooling the bulb in which the nitrogen was condensed. Having obtained a considerable quantity of this light nitrogen it was purified from that gas in the usual manner, and the argon containing helium and neon was liquefied. By fractional distillation it was possible to remove the greater portion of the helium and neon from this mixture of gases, leaving the argon behind. Many attempts were made to separate the helium from the neon. Among these was fractional solution in oxygen, followed by a systematic diffusion of the two gases; but it was not found possible to raise the density of the neon beyond the number 9.16, and its spectrum still showed helium lines. It was not until liquid hydrogen made by an apparatus designed and built by one of us (M. W. T.), had been produced in quantity, that the separation was effected; the neon was liquefied, or perhaps solidified, at the temperature of boiling hydrogen, while the helium remained gaseous. A few fractionations serve to produce pure neon; we did not attempt to separate the helium in a pure state from this mixture.

That these are all monatomic gases was proved by determination of the ratio of their specific heats by Kundt's method; the physical properties which we have determined are the refractivities, the densities, the compressibilities at two temperatures, and of argon, krypton, and xenon the vapour-pressures and the volumes of the liquids at their boiling points.

The results are shown in the table.

The compressibilities of these gases also show interesting features. They were measured at two temperatures—11.2° and 237.3°: the value of P.V. for an ideal and perfect gas at 11.2° is 17,710 metre-cubic-centimetres, and at 237.3° to 31,800. This is, of course, on the assumption that the product remains constant whatever be the variation in pressure. Now with hydrogen at 11.2° C. the product increases with the rise of pressure; with nitrogen, according to Amagat, it first decreases slightly and then increases slightly. With helium the increase is more rapid than with hydrogen; with argon there is first a considerable decrease, followed at very high pressures by a gentle increase, although the product does not reach the theoretical value at 100 atmospheres pressure; with krypton the change with rise of pressure is a still more marked decrease, and with xenon the decrease is very sudden. At the higher temperature the results are more difficult to interpret; while nitrogen maintains its nearly constant value for P.V., helium decreases rapidly, then increases, and the same peculiarity is to be remarked with the other gases, although they do not give the product of P.V. coinciding with that calculable by assuming that the increase of P.V. is proportional to the rise of absolute temperature.

These last experiments must be taken as merely preliminary; but they show that further research in this direction would be productive of interesting results.

The spectra of these gases have been accurately measured by Mr. E. C. Baly, with a Rowland's grating; the results of his measurements will shortly be published. It may be remarked, however, that the colour of a neon-

* Abstract of a Paper read before the Royal Society, November 15, 1900.

	Helium	Neon	Argon.	Krypton.	Xenon.
Refractivities (Air = 1)	0.1238	0.2345	0.968	1.449	2.364
Densities of gases (O = 16) ..	1.98	9.97	19.96	40.88	64
Boiling-points at 760 m.m. ..	?	?	86.9° abs.	121.33° abs.	163.9° abs.
Critical temperatures	?	Below 68° abs.	155.6° abs.	210.5 abs.	287.7° abs.
Critical pressures	?	?	40.2 metres.	41.24 metres.	43.5 metres.
Vapour-pressure ratio	?	?	0.0350	0.0467	0.0675
Weight of 1 c.c. of liquid	?	?	1.212 grms.	2.155 grms.	3.52 grms.
Molecular volumes	?	?	32.92	37.84	36.40

tube is extremely brilliant, and of an orange-pink hue; it resembles nothing so much as a flame, and it is characterized by a multitude of intense orange and yellow lines; that of krypton is pale violet, and that of xenon is sky-blue. The paper contains plates showing the most brilliant lines of the visible spectrum.

That the gases form a series in the periodic table, between that of fluorine and that of sodium, is proved by three lines of argument:—

- (1). The ratio between their specific heats at constant pressure and constant volume is 1.66.
- (2). If the densities be regarded as identical with the atomic weights, as in the case with diatomic gases such as hydrogen, oxygen, and nitrogen, there is no place for these elements in the periodic table. The group of elements which includes them is:—

Hydrogen.	Helium.	Lithium.	Beryllium.
1	4	7	9
Fluorine.	Neon.	Sodium.	Magnesium.
18	20	23	24
Chlorine.	Argon.	Potassium.	Calcium.
35.5	40	39	40
Bromine.	Krypton.	Rubidium.	Strontium.
80	82	85	87
Iodine.	Xenon.	Cæsium.	Barium.
127	128	137	137

(For arguments in favour of placing hydrogen at the head of the fluorine group of elements, see Orme Masson, *CHEMICAL NEWS*, 1896, vol. lxxiii., p. 283).

- (3). These elements exhibit gradations in properties such as refractive index, atomic volume, melting-point, and boiling-point, which find a fitting place on diagrams showing such periodic relations. Some of these diagrams are reproduced in the original paper. Thus the refractive equivalents are found at the lower apices of the descending curves; the atomic volumes, on the ascending branches, in appropriate positions; and the melting- and boiling-points, like the refractivities, occupy positions at the lower apices.

Although, however, such regularity is to be noticed, similar to that which is found with other elements, we had entertained hopes that the simple nature of the molecules of the inactive gases might have thrown light on the puzzling incongruities of the periodic table. That hope has been disappointed. We have not been able to predict accurately any one of the properties of one of these gases from a knowledge of those of the others; an approximate guess is all that can be made. The conundrum of the periodic table has yet to be solved.

THE ANALYSIS OF URANIUM AND VANADIUM ORES.

By OLIVER P. FRITCHLE.

THIS scheme for the determination of uranium and vanadium is particularly adapted to the mineral carnotite, which is principally a hydrous potassium uranium vanadate. Both uranium and vanadium can be reduced to their lower oxides in a sulphuric acid solution, with metallic aluminum, and then again oxidised to their higher oxides with a solution of potassium permanganate.

Weigh into a 6-oz. flask $\frac{1}{2}$ gm. of the finely powdered ore, moisten with a few drops of water, add 10 c.c. of nitric acid, and digest at a slow boiling temperature for about one hour. Remove from the source of heat, dilute with 10 c.c. of water, add gradually to neutralisation a saturated solution of Na_2CO_3 , and then 5 c.c. excess; then add 20 c.c. of a 20 per cent solution of NaOH. Boil slowly for about half an hour, and then allow the precipitate to settle until the supernatant liquid is clear.

The uranium, vanadium, and iron are all precipitated by

the sodium carbonate, but on adding a moderate excess of sodium carbonate and a large excess of NaOH, the vanadium is dissolved, while the uranium and iron remain insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydrate in the presence of an iron salt.

Filter off the precipitates of iron and uranium, and wash a few times with a solution of NaOH. Do not wash with water, as it washes the uranium precipitate through the filter. The filtrate should show no uranium on testing a nitric acid solution with potassium ferrocyanide. The filtrate contains all of the vanadium, and it could be determined from this solution were it not for the fact that so large a volume of salt solution is difficult to evaporate, and displace with sulphuric acid without violent bumping and considerable loss by spattering. Furthermore, V_2O_5 is not easily soluble in nitric acid, and only by long digestion is all of the vanadium obtained in solution. Therefore it is more expedient to determine the vanadium in a separate sample as given below.

Dissolve the precipitates on the filter with 20 c.c. of hot dilute nitric (1:1), letting the solution run into the original flask. Dilute the solution with about 40 c.c. of water, add NH_4OH until a slight permanent precipitate forms; then add 40 c.c. of a saturated solution of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, freshly prepared and heated slightly to remove any excess of CO_2 . Uranium is easily soluble in an excess of ammonium carbonate, and the iron is insoluble. Heat to boiling a few minutes, but do not boil, as the ammonium carbonate will be decomposed, and the uranium precipitated by the ammonia. Filter off the iron precipitate, and wash well with a 2 per cent solution of ammonium carbonate. The filtrate contains all of the uranium, and should not show a trace of vanadium by testing with hydrogen peroxide in a nitric acid solution. A red colouration shows the presence of vanadium. Add slowly 20 c.c. of dilute sulphuric (1:1), and boil until dense white fumes are given off. Cool, dilute to about 100 c.c., add about 4 sq. in. of sheet aluminum, cut into half a dozen stripes, and boil for half an hour or until the yellow solution is reduced to a sea-green colour. Fill the flask with water, decant into a No. 4 beaker, and titrate the uranous solution, hot, with a standard solution of potassium permanganate. The iron equivalent of the permanganate, multiplied by 120/56, will give the amount of uranium in the $\frac{1}{2}$ gm. sample.

Dissolve the iron precipitate with hot dilute HCl, add 10 c.c. sulphuric acid, boil to white fumes, cool, dilute, reduce with metallic aluminum, dilute, decant into a beaker, and titrate with the standard solution of potassium permanganate.

The vanadium is determined in a separate sample as follows:—Weigh into a 6-oz. flask $\frac{1}{2}$ gm. of the ore, add a few drops of water, 10 c.c. nitric acid, and 10 c.c. sulphuric acid. Boil until the nitric acid is all expelled, and dense white fumes of sulphuric acid are evolved. Cool, dilute, add aluminum, and reduce the uranium, vanadium, and iron by boiling for half an hour. Fill the flask with water, decant into a beaker, and titrate, hot, with the standard solution of potassium permanganate. The number of c.c. of permanganate, less the number of c.c. required for the uranium and iron, is the permanganate required to oxidise the vanadium, which, multiplied by $51.1/112$, gives the amount of vanadium in the $\frac{1}{2}$ gm. sample.

The end reaction of vanadium is slow, and permanganate must be added slowly until a permanent pink is obtained.

I prefer the use of aluminum to either zinc or sulphurous acid as a reductor. In the case of vanadium, if sulphurous acid is used, the vanadium is not reduced as low as when aluminum is used, being reduced only to the blue colour, and requiring, approximately, half the amount of potassium permanganate.

The volumetric estimation of vanadium by potassium permanganate is a beautiful titration, changing from purple through blue, green, and yellow to pink.—*The Engineering and Mining Journal*, November 10, 1900.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART V.

By HARRY BREARLEY.

(Concluded from p. 247).

SILICON (continued).

II. THE ESTIMATION OF SILICA IN REFRACTORY MATERIALS.

715. CAMERON (C. N., lxi., 171).—After fusion all evaporations should be made with HCl not H_2SO_4 . One evaporation does not make all the SiO_2 insoluble. The influence exerted by Fe, Al, Ca, and organic matter is observed.
716. CRAIG (C. N., lx., 227).—On account of imperfect dehydration of SiO_2 and contamination of precipitates with soda salts, fusion is undesirable. Drive off SiO_2 with HF and H_2SO_4 . A simple apparatus for purifying HF. (See 736).
717. ARCHBUTT (J. S. C. I., 1892, 215).—Confirms 716. The SiO_2 of clays is not completely insoluble after $KHSO_4$ fusion. Filtrate evaporated with H_2SO_4 .
718. ROCHOLL (C. N., xli., 234).—Limestones, siliceous ores, and like minerals are readily decomposable with HCl after strong ignition; the bases already present acting as flux.
719. KERN (C. N., xxxv., 203).—A process for the estimation of SiO_2 , Fe_2O_3 , Al_2O_3 , MnO, CaO, and MgO in fire-clay, &c. Opens out by Na_2CO_3 fusion.
720. ANON. (C. N., v., 228).—Comparative value of fire-bricks determined by heating simultaneously under layer of limestone and observing the degree to which they have been acted upon.

III. THE ESTIMATION OF SILICA IN SLAGS AND SILICATES.

721. ROSE (C. N., i., 179).—Silicates may be decomposed by heating with powdered ammonium fluoride. Also HOFFMAN (C. N., xvii., 94).
722. AVERY (C. N., xix., 270).—Almost any acid with a normal fluoride will completely dissolve silicates; the loss of SiO_2 need only be very slight.
723. KUHLMANN (C. N., xi., 194).—Silicates decomposed in current of HF at dull redness. Necessary apparatus described.
724. STORY-MASKELYNE (C. N., xxi., 27).—Decompose silicate in a special form of platinum apparatus, collect volatile SiO_2 in ammonia, precipitate the neutral solution with KCl and alcohol, and weigh as fluo-silicate.
725. ALLEN (J. C. S., lxx., 575).—A small crucible containing the powdered silicate moistened with H_2SO_4 is placed in a larger one containing $H_2SO_4 + HF$. A dish of cold water placed over the larger crucible causes re-distilled HF to drop into the smaller.
726. FELLEBERG (C. N., xiv., 243).—Fuse with $CaCl_2 + CaO$, leach with water; the solution contains only Ca and the alkalis.
727. GLINKA (J. C. S., lxiv., ii., 491).—Fuse with $CaCO_3$, decompose melt with nitro-hydrochloric acid, and proceed as usual.
728. BONG (C. N., xxxvii., 112).—Silicates are completely decomposed by fusion with Pb_3O_4 at low temperatures. Dissolve melt in HNO_3 , and evaporate for SiO_2 .
729. JANNASCH (C. N., lxxii., 51).—As Bong, but uses lead carbonate.
730. LECLERC (C. N., lxxvii., 27).—As Bong, but does not appear to evaporate before filtering off the "completely insoluble hydrated silica."
731. HEMPEL (C. N., xlv., 81).—Fuse silicate with sub-nitrate of bismuth, dissolve in HCl, and evaporate for SiO_2 .

732. CHATARD (C. N., l., 279).—As Hempel, but uses the oxide.
733. ILES (C. N., xliii., 78).—Decompose by fusion with KHO in Ag crucible. The SiO_2 is washed with ammonia to remove AgCl. (See 219).
734. HOLTHOF (C. N., li., 18).—Fuse with $NaHCO_3$. At the moment of formation of the normal carbonate the base has an intensified affinity for SiO_2 .
735. SHIMER (C. N., lxx., 102).—Spinel (magnesium aluminate), which may occur in blast-furnace slags, is not decomposed by alkaline fusion nor with $HF + H_2SO_4$; it is by $KHSO_4$. (See 741).
736. GILBERT (C. N., lxi., 270 and 281).—Evaporation of fusion with HCl does not make all the SiO_2 insoluble. $CaCl_2$ assists dehydration, but neither CaO nor Al_2O_3 tend to re-form silicates at higher temperatures; MgO does. (See 757).
737. LINDO (C. N., l., 25).—The character of the SiO_2 may be vitreous or amorphous, according to the varying treatment of the alkaline melt with acids.
738. ILES (C. N., l., 194).—Hot slags plunged into cold water are completely decomposed by HCl. Complete analysis of slags; lime is determined in the presence of the iron.
739. JONES (J. I. S. I., 1888, i., 383).—Compares the fusion process and dissolving of chilled (738) samples in HCl. Dehydrates SiO_2 in either case at $120^\circ C$.
740. CAMP (J. I. S. I., 1897, i., 578).—Decompose blast-furnace slags with HCl, and evaporate twice for SiO_2 .
741. MEEKER (J. S. C. I., 1897, 636).— H_2SO_4 dehydrates better than HCl evaporation, but the filtrate cannot be used for the estimation of Ca and Al. Yields good results in the presence of spinel (735).
742. JANNASCH (J. C. S., lxx., 576).—Fuse with boric acid. Boric acid eliminated by evaporation with HCl and methyl alcohol.
743. JANNASCH (J. C. S., lx., 619).—Decomposed by heating with HCl in sealed tubes.
744. WINKLER (C. N., i., 215).—Pyrogenous silicates in fine powder are dissolved by alcohol saturated with HCl.
745. HUTCHINGS (C. N., liv., 173).—A neat qualitative analysis of silicates, chiefly by means of the blow-pipe.
746. FRIEDBURG (C. N., lxii., 22).—A complete analysis (Si, Fe, Al, Mn, Ca, Mg, Ba, Sr, alkalis, H_2O , P, F, and Ti) of insoluble silicates.
747. HILLEBRAND (C. N., lxxviii., 43).—A lengthy review of the analysis of silicate rocks, paying much attention to the elements occurring in small amounts.

IV. MISCELLANEOUS.

748. BARROWS and TURNER (J. C. S., lxi., 551).—Volatilisation of the iron with Cl is not suited to the estimation of slags containing iron compounds; the sample should be decomposed by cupra-sodium chloride. (See 673 and 694).
749. THOMAS (J. I. S. I., 1888, ii., 241).—The percentage of Si in a pig varies; it is higher at the point of a pig than at the butt.
750. PHIPSON (C. N., xi., 278).—Si exists in iron in two states, distinguished by their behaviour with aqua regia.
751. TOSH (C. N., xliii., 145, 178, and 217).—Discredits the existence of Phipson's graphitic silicon, and also the later statement that the two forms are the silicide and silicate.
752. HOGG (J. S. C. I., 1895, 245 and 262).—Is Si capable of existing in two conditions analogous to that of C in the hardened and annealed steels?
753. MORTON (C. N., xxix., 107).—Experiments showing that Si exists in pigs as a silicide of iron. Also JORDON and TURNER (J. C. S., xlix., 215).

754. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—Si exists in iron as silicides intermediate between Fe_3Si_2 and Fe_2Si , but it combines with Mn in preference to iron.
755. SKEY (*C. N.*, xvi., 187).— SiO_2 thrown down by evaporation with HCl can retain small amounts of P.
756. HAUTEFEUILLE (*C. N.*, i., 272).— SiO_2 should not be dehydrated in the presence of phosphoric acid above 100°C .
757. LORD ("Metall. Anal.," p. 13).—In the presence of CaCl_2 dehydrate SiO_2 at 100°C ; higher temperatures may cause the SiO_2 to re-combine with the bases. (See 736).
758. LAUFER (*C. N.*, xxxvii., 162).—By melting a silicate with a salt of P, the metallic oxides are dissolved, but not the quartz; separate amorphous SiO_2 with NaHO .
759. LUNGE (*J. S. C. I.*, 1897, 762).—Aqueous soda attacks quartz; Na_2CO_3 is better for separating amorphous silica.
760. MICHAELIS (*J. S. C. I.*, 1895, 1065).—Boiling 10 per cent Na_2O does not attack quartz. Quartz in clay is often so finely divided as to pass through filter-paper.
761. CARON (*C. N.*, v., 102).—The only acids which attack crystallised silicon are nitro-fluoric.
- 761a. NEWTH (*J. S. C. I.*, 1895, 1074).—Crystallised Si burns in HF gas at a moderate temperature.
762. FRESSENIUS and HINTZ (*C. N.*, lx., 85).—Cryolite is analysed by heating with H_2SO_4 in a leaden tube; the volatile fluorides are absorbed in ammonia. For other means of estimating Si when F is present see Hampe (*J. C. S.*, lxii., 1127), Reich (*J. C. S.*, lxx., 531), and Stahl (*J. C. S.*, lxx., 621).
763. HIRSCHWALD (*C. N.*, lxii., 24).—Microcosmic fusion is of doubtful analytical significance, because SiO_2 is appreciably soluble in the head of the double salt.

THE PLASTICITY OF SOLID BODIES, AND ITS CONNECTION WITH THE FORMATION OF ROCKS.

By W. SPRING.

(Concluded from page 249).

It often happens that the volume of the product of combination of two or more bodies is less than the sum of the volumes of the uncombined elements. For example, the formation of sulphide of silver is accompanied by a contraction of 6·3 per cent of the volume of its elements. The contrary occurs but rarely; for example, the hydrated sulphide of arsenic is 4·8 per cent greater in volume than the sum of the water and of the anhydrous trisulphide of arsenic. Now, if we compress a mixture of elements in a state to give a compound of the first type, we notice that pressure assists the chemical reaction the more, as the reciprocal solubility of the two elements is the more pronounced. For example, silver and sulphur combine well under pressure: they also combine when they are heated together. On the other hand, zinc and sulphur—which may be melted together without, so to speak, forming sulphide of zinc—hardly combine any better under pressure, while the contraction resulting from the combination amounts to nearly 5 per cent of the volume of the elements. We have made a large number of compounds of the first type with the aid of compression, especially sulphides and arsenides. The old chemical adage, *Corpora non agunt nisi fluida*, can no longer therefore be taken as literally true; it is the speed of the reaction which depends principally on the fluidity of the substance, but not the faculty of reacting.

It is easy to foresee what will be the effect of compression on compounds of the second type; there is not only no trace of reaction, but the compound is decomposed. The hydrated sulphide of arsenic is resolved into anhydrous sulphide and water; cupro-calcic acetate, which is more voluminous than its components, gives acetate of copper, acetate of calcium, and water.

In the same way several substances in an allotropic state have been changed into a more dense form; for instance, prismatic sulphur was easily converted into the octahedric variety, and amorphous arsenic became crystalline. These facts received a remarkable confirmation when M. Moissan showed that if the crystallisation of carbon dissolved in melted iron takes place under sufficient pressure, small diamonds are formed. There is another fact connected with these results; experiment has shown that compression only produces a permanent diminution in the volume of a solid body, when this latter allows of the formation of a more dense allotropic condition. When this condition does not exist, compression only diminishes the volume of the solid during its application. Thus solids behave in the same way as liquids and gases, and have as perfect an elasticity, and there is nothing, moreover, which authorises the opinion that one chemical element can be transformed into another denser one by mechanical means.

All these results show why compression alone of sedimentary deposits has not been able to cause the solidification of rocks. But Nature has probably put into force a factor of which we have not yet taken notice, namely, moisture. We know that the solubility of many bodies in water is increased by pressure; may we not ask whether bodies apparently insoluble, like sand, may not give some signs of dissolution when strongly compressed in contact with water. We have therefore made experiments in this direction, the results of which may be summed up as follows:—In the same manner as with compound bodies, the volume of a solution is hardly ever the exact sum of the volume of the solvent and of the body dissolved; as a rule it is less. Now all bodies which fulfil this condition unite incomparably better in a moist state than in a dry state; the reason is that their solubility increases with pressure, the solvent becomes charged with matter, and forms a supersaturated solution at the ordinary pressure. When the pressure ceases, the excess of matter dissolved is deposited on the remainder of the solid and cements the grains together; it is, in fact, a true *setting*, such as occurs with plaster. On the other hand, bodies, of which the solution is accompanied by an increase of volume, unite with difficulty when moist under pressure, because the solvent re-dissolves the material when the pressure ceases.

Again, bodies which are generally considered to be insoluble in water, such as hydrate of iron, peroxide of manganese, various carbonates, &c., join better when wet than dry. We have obtained agglomerations the surface of which presented an extremely interesting appearance, being vitreous and transparent, and seeming to point to the commencement of liquefaction. Carbonate of copper showed this to a remarkable degree; though the interior of the block preserved the pale green colour of the powder, the surface seemed to be covered with a layer of malachite, green and transparent. It recalled the slipping surfaces of our older rocks. We may therefore suppose that the grains of sand or gravel, in "banket" for example, become covered with a supersaturated solution of silicic acid by the action of pressure, and that this solution in unstable equilibrium has furnished the cement necessary for solidification. It is not without interest to remark that there really exists between the grains of sand and gravel in banket, a siliceous layer which escapes general notice. Silicic acid, however, even in the solid state, has the property of dissolving in a solution of potash or soda, while the quartzose grains are refractory and are only attacked with extreme slowness. A block of banket should therefore become disintegrated in an alkaline

solution. Experiment confirms this deduction; conglomerates of recent formation required only a few weeks to disintegrate at the temperature of boiling water; older rock formations offered a greater resistance to alkalis. They only became friable, while the former was reduced to sand. The reason of this greater resistance may be found in the fact that the silicic acid has, in the course of time, passed more completely into the quartzose state which is refractory to potash.

We must not, however, think that these last observations solve the problem. There are, in fact, some compact rocks which have never been subjected to enormous pressures, that is, anything approaching 70 tons. It is therefore necessary to try whether the simple infiltration of a silicic solution can cement the particles through the slow evaporation of the water of solution. For this purpose we tried to cement sand together by means of a solution of silicic acid. We know that a solution of this acid submitted to slow, spontaneous desiccation, forms a vitreous mass of great hardness. We therefore made a paste of sand and silicic acid, and allowed it to dry. There was not a trace of agglutination. The reason of this discouraging result was seen at once on making a microscopic examination of the substance. The silicic acid had, in fact, adhered to the grains of sand, but, owing to the enormous contraction which accompanied the desiccation, it cracked in every direction round the grains. The cause of the failure being known, its remedy was apparent. By the application of a slight but continuous pressure we obtained a commencement of solidification. If the result was not entirely satisfactory, at any rate it proved the possibility of obtaining perfect results, by suitably varying the conditions and allowing time to play a more important part.

The solidification of rocks may then have taken place in Nature, after the infiltration of siliceous waters accompanied by a compression of relatively low intensity, but lasting a long while. The co-operation of these factors seems to be indispensable, as pressure alone, like infiltration alone, is inefficacious, as far as one may conclude from laboratory experiments.

The solidification of calcareous rocks may also be explained by the above process; the *débris* of shells impregnated with a solution of acid calcic carbonate, has become cemented together on the escape of the carbonic acid, by diffusion into the atmosphere, and by the slow crystallisation of the dissolved calcareous matter, in greater proportion as the pressure was increased.

Finally, even if the phenomenon of regelation, mentioned at the commencement of this article, is not confined to ice, it has not, at any rate, played a part in the formation of rocks in any way approaching that which it played in the history of glaciers.—*Revue Générale des Sciences*, Sept. 30, 1900.

A NEW REACTION FOR THE DETECTION AND ESTIMATION OF SMALL QUANTITIES OF NITROUS ACID.

By H. ERDMANN.

It has been known for the last twelve years that the addition of mineral acids to cultures of the cholera bacillus gives rise to the formation of a violet colouration (Brieger, *Deutsche Medicinische Wochenschrift*, 1887, 303 and 469). Bujvid, who has examined this reaction in a more detailed manner, has found that it is due to the formation of coloured salts with a characteristic base. This latter can be isolated in the form of reddish-brown flakes by shaking the violet solutions, previously made alkaline, with benzene.

By dissolving this "cholera-red" in concentrated sulphuric acid, and then pouring the solution into dilute

soda, it is easily transformed into a new colouring base, "cholera-blue." The first of these substances is converted into indol by distillation with powdered zinc. E. Salkowski (*Virchow's Archiv*, cx., 366), has shown that the choleraic bacteria are constantly producing nitrous acid, and that the phenomena of colouration observed in cultures of these bacilli is nothing else than a known reaction of nitrous acid (Wencki, *Berichte*, viii., 727).

It has been recognised later on that this latter is a product elaborated by the numerous bacteria belonging especially to the series of pathogenic anaerobes. It follows from this observation that the presence of nitrous acid in certain media, particularly in potable waters, should be considered as an indication of the presence of such and such bacteria, if it is desirable to form an opinion on the spot without the aid of any special apparatus; the above mentioned method, however, still leaves much to be desired.

In his experiments on spring or well-waters used for drinking purposes by either man or beast, the author takes into consideration quantities of nitrite which, on an average, correspond to a normal solution of one millionth, so that a solution of 100,000th would indicate a microbial activity of considerable power. It is only under very exceptional circumstances that the bacillary production of nitrite would lead to a concentration corresponding to a normal solution of a 10,000th; he has therefore taken no notice of solutions of less strength than 1 centigram. of nitrous acid per cubic metre. For proportion varying from 1 centigram. to 1 gram. per cubic metre, it is indispensable to make a quantitative estimation, at least approximately, if we wish to know whether the water under examination must be condemned, or looked upon with more or less suspicion.

It is easy to see how insufficient are the usual methods used for this purpose by referring to the words of Fr. Erismann. (Lunge, *Untersuchungsmethoden*, i., 728), in the last edition of Böeckmann's book:—"It is rarely necessary to estimate the nitrous acid in the analysis of waters used for drinking or domestic purposes. A really pure water should not contain any nitrous acid, and those which contain more than mere traces must be looked upon as containing impurities of such a nature as to render them unfit for drinking."

It is therefore interesting from the practical point of view to determine the quantitative value of these "traces" of nitrite. The appearance of certain waters which are dangerous, both for man and beast, is often excellent, even when their proportion of nitrite has reached the upper limit (1-2 grms. of nitrous acid per cubic metre). On the other hand, it is not permissible to establish the character of water, as is often done, on its richness in chlorine, as the salt is often derived from mineral or saline deposits of considerable extent.

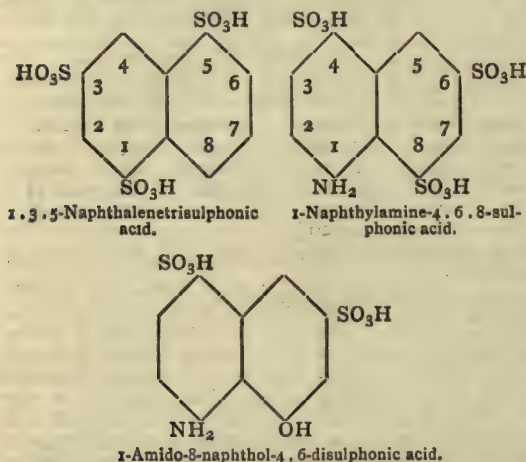
If we can succeed in transforming the nitrous acid of a water integrally into a strongly coloured azoic compound, it would be possible to base an examination at once qualitative and quantitative on the intensity of the colouration obtained. (See Annaheim, *Berichte*, ix., 1151).

It is necessary to avoid the use of phenylenediamines (see Griess, *Berichte*, xi., 624), and of analogous bodies which give insufficiently characteristic brown colourations. These compounds are, further, too sensitive to the action of oxidising agents, with which they give rise to colouration phenomena analogous to those which are caused by nitrous acid under the same conditions.*

As a result of numerous preliminary experiments the author has decided to use 1.8-amino-naphthol-4.6-disul-

* For the same reason the use of the starch-iodine method cannot be allowed (see Kaemmerer, *Zeit. f. Analyt. Chem.*, 377), which is unfortunately too often used in bacteriological laboratories. In the present state of the water question, we must take notice of the possible presence, not only of oxide of iron, but also of free chlorine, ozone, and other oxidising agents. When submitted to the action of iodide of starch, a water which had been completely disinfected by one of these substances, would behave in such a manner as to be looked upon with suspicion.

phonic acid obtained from 1.3.5-naphthalene-trisulphonic acid (*Berichte*, xxxii., 3186), by nitration, reduction, and treating with boiling caustic soda (*Ch. Ind.*, 1898, p. 523; *Lehne's Färbertsg.*, x., 358).



This acid has the property of combining very easily with the diazo derivatives in acid solution, giving rise to monoazoic colouring materials which, by their solubility, great tinctorial power, and characteristic colour, are perfectly adapted for the object it is desired to attain. The operation is carried out in the following manner:—

50 c.c. of the water to be examined are mixed with 5 c.c. of a hydrochloric solution of sulphanilic acid (2 grms. of sulphanilate of soda per litre), and after the lapse of ten minutes, as the dinitration does not take place instantaneously in very dilute solutions, about 0.5 grm. of 1-amino-8-naphthol-4,6-disulphonic acid is added in the solid state, and in the form of an alkaline salt.

In the presence of nitrous acid a wine-red colour is produced which reaches its maximum intensity in about an hour. For quantitative estimations the shade obtained is compared with a series of tubes of known strength prepared at the same time.

For this purpose we make use of normal solutions of nitrite at a millionth, one hundred-thousandth, and one ten-thousandth. When we have to make really exact measurements, these solutions must be prepared at the last moment by diluting the normal solution, as, in such dilute solutions, there soon develop micro-organisms, whose activity would gradually diminish the proportion of nitrous acid present. It is for this reason that a diminution takes place in the quantity of nitrous acid in impure waters which have been kept too long. However, a spring water, which had been the cause of an outbreak of malignant pustule, still gave a distinct colouration with the reagent in question, after the lapse of a year. It must therefore be admitted that nitrous acid can be detected long after the disappearance of the micro-organisms by which it was produced. This property gives the chemical examination of water a distinct advantage over the bacteriological method, by which, on account of the ephemeral life of anaërobic bacteria in water, we are rarely able to isolate them in an effective manner.

Among the methods of investigation previously known that of Griess (*Berichte*, xii., 427), must be mentioned; it is based on the use of α -naphthylamine. Although fairly sensitive this method is not very applicable to the object we have in view. In the first place, the reagent used is rarely colourless, and it is difficult to keep. Another drawback is met with in the slight solubility of the yellow-red colouring material, which in the examination of hard or saline waters, is deposited in a flocculent state. It follows that this phenomenon seriously interferes with quantitative estimations. The author cannot give an

opinion on the use of this reagent for the detection of nitrosylsulphuric acid in sulphuric acid (Lunge and Luoff, *Zeits. f. Angewandte Chem.*, 1894, 348), as he has never made any experiments on the subject. But as far as concerns the analysis of waters, he considers it insufficiently exact and characteristic. Riegler's method (*Zeits. f. Anal. Chem.*, xxxv., 677, 377; Koenig, *Untersuchenland. u. Gew. Wichtiger Stoffe*, Second Edition, 1898, 610), is even less able to bear comparison with the new method; in fact, naphthionic acid, like many other easily diazotable substances which the author has experimented with, possesses a fluorescence which interferes disadvantageously with the reaction.

Solutions of 1-amino-8-naphthol-4,6-disulphonic acid are not at all dichroic under the existing conditions. Oxidising agents, such as perchloride of iron, cause the formation of a yellow colouration. It is impossible, however, to confound this latter with the bright wine-red shade on which the new method depends.

The Laboratory of Applied Chemistry, "Halle-a-S., Domplatz, 1," will supply samples of the new reagent ready for use, gratuitously to those interested in the matter. Instead of using solutions of nitrite of known strength as standards of comparison, a coloured paper scale paper may be used for colorimetric comparison, — *Berichte*, vol. xxxiii., p. 210.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 251).

Dilatometer Experiments (continued).

Experiment 30.—A continuation of Expt. 29. Starting from vitreous selenium, the temperature was rapidly raised, and in this case attained almost 175° before the transformation began. The subsequent readings are as follows:—

Temp.	Scale.	Time.
175°	390	9 : 39
186	397	9 : 40
195	395	9 : 41
203	405	9 : 47
199	393	11 : 20

This confirms the results of Experiment 29.

The tube was next heated to 225° to effect fusion, and then cooled to 125° to observe the nature of the transformation at that point. The readings are:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
232°	560	11 : 45	176°	310	12 : 43
125	265	12 : 03	—	311	1 : 01
127	231	12 : 16	198	377	1 : 30
—	177	12 : 32	206	399	1 : 50
—	177	12 : 37			

The transformation at 125° brings the dilatometer back to a reading almost identical with that obtained by interpolation from the results of Experiment 28, where the dilatometer contained selenium which had been changed over at 200° and then cooled down.

In the experiments which follow, special care was taken to eliminate water from the system. The paraffin used in all these later experiments was dried by sodium. For drying selenium which has been precipitated out of an aqueous solution of selenious acid, it is by no means sufficient to heat it for an hour or two at 120°, although by this means it goes over to the metallic form, and one would suppose that such a change would be likely to set free all the moisture present; on fusing such a preparation in a tube, however, a very considerable quantity of water is still given off. The material here used was dried by heating to 230° for some time in an exhausted Λ -shaped

* From the *Journal of Physical Chemistry*, vol. iv.

tube, containing sulphuric acid in the other arm. By observing these precautions, and by occasionally opening the dilatometer tube to permit the escape of the small bubbles which had developed in the bulb, it was possible to get very concordant results. These experiments confirm the earlier ones.

Experiment 32.—New dilatometer.* Starting from metallic selenium, the following observations were made:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
84°	51		223°5	562	3 : 32
153	243		200	477	3 : 36
196	361	2 : 51	192	428	3 : 46
204	386	3 : 06	198	374	3 : 59
219	430	3 : 12	196	362	4 : 11
228	525	3 : 19			

Here the last reading at 196° accords almost exactly with the first. The material was again fused and then rapidly cooled; on heating up again, the transformation began at about 130° and gave, after coming to rest at 191°, a reading of 355, which accords very closely with the above value of 362 at 196°.

Experiment 36 was made with a new dilatometer. The level at 199° corresponding to the more dense form, was 321 on the scale. After fusion and cooling, it was placed in a bath at 200°; the transformation took place very rapidly, and the level came to 322 at 199°, from which there was no further change during five minutes. The material was again fused and cooled, and then placed in a bath of boiling water until the change was almost completed; it was then replaced in a 200° bath, where it gave a reading of 314 at 197°. The selenium was again fused and cooled down. This time it was placed in a cold bath, whose temperature was then rapidly raised—this being the method by which Siemens prepared his light-sensitive selenium cells. The change began at about 120° and the temperature, after reaching 200°, was maintained for some time at that point; the dilatometer gave a final reading of 321° at 200°. On being transferred to a bath of boiling water, it gave a reading of 36 at 99°. The material was once more fused and then placed directly in the water-bath; the final reading was 44, and as the change proceeds very slowly towards the end, this may reasonably be taken as a trifle too high. Finally, the temperature was raised to 200° and then lowered to 80°; all the readings so obtained were found to lie along one line, and there was nowhere any sign of a change. This line cuts 100° at a little above 40, and 200° a little above 320°.

In order to make sure that the denser form which plays so important a part in these dilatometer experiments was really metallic selenium, the material was removed from this last bulb and its specific gravity determined; the value found was 4.77.

Experiment 36 shows that metallic selenium is the only form which results from the transformation of the vitreous modification, whether at 100° or in a bath whose temperature is rapidly raised to 200°. The readings obtained at 200° are the same in each of these two cases, and are identical with that obtained by holding fused selenium at 200° until the transformation is complete.

Experiment 41.—This was a further attempt to get some indication of a reverse change from the grey metallic into a less dense form, below 100°. Starting from vitreous selenium, the following readings were taken:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
59°	114	11 : 15	80°	134	1 : 20
62	118	11 : 18	81	96	2 : 30
68	130	11 : 27	—	66	4 : 06
74	141	11 : 40	70	47	4 : 15
81	154	12 : 16	69°5	45	4 : 35
83	157	12 : 25	98	92	4 : 45
82	153	12 : 35	—	84	5 : 05

* In the later experiments, a side tube was set on, at an angle, to the bulb of the dilatometer; this facilitates the filling, and can be sealed off afterwards.

The experiment shows that when the change has proceeded some distance at 81°, and the temperature is lowered to 70°, there is no sign of a recovery during twenty minutes, although the last two readings show that the transformation was not complete, *i.e.*, that two forms were present.

Experiment 43.—Confirmatory of Experiment 41. This determination, which was carried on in a dilatometer filled with quinoline, yielded the following readings:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
81°	112	2 : 08	70°	42	4 : 15
—	93°5	2 : 15	69°5	41	4 : 35
—	74	2 : 40	98	71	4 : 48
—	56	3 : 36	—	66	5 : 05
—	52°5	4 : 06			

Experiment 45.—Carried on with the same dilatometer that was used in Experiment 41. Starting from vitreous selenium, these readings were made:—

Temp.	Scale.	Time.	Temp.	Scale.	Time.
65°	127	12 : 32	78°5	150°5	2 : 03
71°5	139	1 : 10	80	152	2 : 16
74	143	1 : 32	81°5	152	2 : 34
77	148°5	1 : 51	78	139	3 : 07

showing that the transformation began at about 80° in this case. The temperature was then raised—

Temp.	Scale.	Time.
107°	178	3 : 36
125	150	3 : 38
130	122	3 : 39
156	158	

Then the dilatometer was placed in the cooler bath—

Temp.	Scale.	Time.
67°5	19	3 : 51
—	17	4 : 15

The dilatometer then stood over night, and registered on the following day—

Temp.	Scale.
58°5	0

Four days later the level was again taken—

Temp.	Scale.	Time.
63°	5	11 : 30
78	28	12 : 40

The bulb then remained at ordinary temperatures for two weeks, sometimes standing for half a day in direct sunlight. At the end of that time a reading was again taken and gave—

Temp.	Scale.
59°	0
69	15

and after standing in sunlight for a few hours more, it gave on the following day—

Temp.	Scale.
70°	17

Two months later a reading was again taken, and gave at—

Temp.	Scale.
63°	4

which shows that no change had taken place.

This experiment illustrates the complete stability of metallic selenium at ordinary temperatures and up to 60°, whether it be kept in diffused daylight or in direct sunlight.

When selenium is heated by itself to 100° it does not always go over entirely to the metallic form. Petersen (1891) found that specimens of selenium which were transformed from the vitreous into the metallic form, at whatever temperature, always contained more or less of the original material. This is illustrated by the following experiment:—

Experiment 46.—A quantity of vitreous selenium was heated for half an hour in a water-bath, and was then

placed in a dilatometer with quinoline. The following are the readings:—

Temp.	Scale.	Time.
74°	103	1 : 32
80	92	2 : 16
78	78	3 : 00
73	70	3 : 21
67.5	63	3 : 45

The dilatometer was, later on, heated for five hours between 45° and 60° and showed no signs of a reverse transformation, although raising the temperature afterwards to 80° showed that the transformation had not been entirely completed.

When vitreous selenium is placed in a dilatometer with water, the transformation begins at about 80° and proceeds slowly—but uninterruptedly—to an end, as shown by the following experiment:—

Experiment 69.—3.06 grms. of vitreous selenium were placed in a dilatometer provided with a capillary arm previously calibrated. The following readings were made:—

Temp.	Scale.	Time.
64°	89	11 : 44
71	98	12 : 14
77	106	12 : 30
79	108.5	12 : 35
81	111	12 : 40

A slight transformation took place at this last temperature, and the experiment was continued on the following day.

Temp.	Scale.	Time.	Temp.	Scale.	Time.
67°	86		80°	65.5	12 : 06
82	102.5		79	58.5	12 : 40
85.5	105	11 : 05	81	42.5	2 : 15
84	87	11 : 28	80	36	4 : 20
83	81	11 : 36			

and on the following day—

Temp.	Scale.	Time.
79°	27	11 : 20
80	26	12 : 30
—	24	3 : 30
77	21	5 : 10

The transformation may be taken as complete.

Calculating the change in density from the difference between the original and final readings at 77°, and assuming the density of vitreous selenium to be 4.3, we find for the density of the metallic form by this experiment 4.77. The determination shows that no other forms make their appearance here but the two mentioned.

In another experiment, also carried on in water, a quantity of selenium was heated in a water-bath for one and one-half hours, after which no further change of volume could be noted. The mass had the familiar steel grey colour. On raising the temperature to 130° no change took place. Some of it was then taken out, and placed in a dilatometer containing aniline, and heated during one and one-half hours to about 150°. This also brought about no further change, showing that in water as well as in other liquids, it is the metallic form which always results from a transformation of the vitreous modification no matter at what temperature this transformation is effected.

(To be continued).

Messrs. F. E. Becker & Co. have just issued a new Illustrated Catalogue of Physical Apparatus, fully illustrating and describing Magnetism, Frictional Electricity, Voltaic Electricity, Electro-magnetism, Electro-plating, and "X" Ray Work, &c. The catalogue is well printed and the illustrations are of good character, and we recommend its perusal to anyone who may be about to fit up or extend a physical laboratory.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

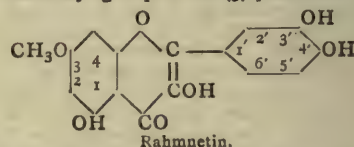
Ordinary Meeting, November 1st, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

(Concluded from p. 254).

139. "Rhamnazin and Rhamnetin." By A. G. PERKIN and J. R. ALLISON.

In rhamnazin (quercetin dimethyl ether) the position of but one methoxyl group is known (*Trans.*, 1897, lxi., 818), whereas that in rhamnetin (quercetin monomethyl ether) (Herzig, *Monatsh.*, 1888, ix., 548) has not been determined with certainty. On gentle decomposition, rhamnazin, rhamnetin, and quercetin tetramethyl ether give the same phloroglucinol derivative, as in each case the latter reacts with diazobenzene to form a compound, occurring in orange-red needles, m.p. 251–252°. This is *diazobenzenephloroglucinol monomethylether*. (Found C=65.17; H=4.64; N=15.57; CH₃=4.40 per cent); consequently rhamnazin is methoxyrhamnetin, and both contain a methoxyl group in the (3) position.



140. "Luteolin." III. By A. G. PERKIN and L. H. HORSFALL.

On methylation, luteolin (from weld) yields two ethers insoluble in alkali, (a), m.p. 191–192° (*Trans.* 1896, lxi., 206), and a more soluble compound, (b), newly isolated, m.p. 161–163°. The latter, C₁₅H₇O₃(OCH₃)₃, is the true *luteolin trimethyl ether*, for on decomposition it forms *veratric acid* and *phloroglucinol monomethyl ether* (identified as its diazobenzene derivative, m.p. 251–252°). The ether (a), m.p. 191–192°, appears to be *methyl luteolin trimethyl ether*, due to the existence of a methyl group entering the ring during methylation, or less probably to the presence of methyl-luteolin in weld. On gentle decomposition, *veratric acid*, and a crystalline *phloroglucinol* derivative result, the latter yielding with diazobenzene, a derivative, in orange-coloured needles, m.p. 198–200°, C₈H₈O₇(C₆H₅N₂)₂, apparently *diazobenzenemethyl phloroglucinol monomethyl ether*. *Acetyl methyl luteolin*, colourless needles, melts when rapidly heated at 238–240°. Luteolin from the *Genista tinctoria* behaves similarly on methylation. The monopotassium and sodium salts of luteolin have now been crystallised, and have the respective compositions KC₁₅H₉O₆ and NaC₃₀H₁₉O₁₂. Weld contains a trace of another colouring matter C₁₅H₁₀O₅, which, on decomposition with alkali, yielded *p-hydroxybenzoic acid*, a trace of *protocatechuic acid*, *phloroglucinol*, and *p-hydroxyacetophenone*. By further reactions, it was identified as *apigenin*. By the gentle action of alkali, morin, a colouring matter of *Morus tinctoria*, yields, in addition to β -resorcylic acid and *phloroglucinol* (*Trans.*, 1896, lxi., 697), previously found, some quantity of β -resorcylic aldehyde.

141. "Genistein." II. By A. G. PERKIN and L. H. HORSFALL.

Genistein dimethyl ether, m.p. 137–139° (*Trans.*, 1899, lxxv., 835) yields a monacetyl derivative, m.p. 202–204°, C₁₄H₇O₂(OCH₃)₂C₂H₃O, and on gentle decomposition gives *p-methoxyphenylacetic acid* and *phloroglucinol monomethyl ether*, identified as its diazobenzene derivative, m.p. 251–252°. The second product of the methylation, m.p. 200–202° (previously given as 187–189°), appears to be a *methylgenistein dimethyl ether* (compare luteolin). It forms a monacetyl derivative, C₁₇H₁₅O₅·C₂H₃O, m.p. 212–214°, and on decomposition gives *methoxyphenyl-*

acetic acid and a phloroglucinol derivative whose diazo-benzene compound (probably *diazobenzene methylphloroglucinolmonomethyl ether*), orange-coloured needles, melts at 198–200°. This is identical with that produced from methyluteolintrimethyl ether. *Genistein diethyl ether*, $C_{14}H_{18}O_3(OEt)_2$, colourless needles, m. p. 132–134°, and its monacetyl derivative, m. p. 168–170°, have been obtained. On decomposition it gives *p*-ethoxyphenylacetic acid and a phloroglucinol compound. These results are in harmony with the constitution of a *trihydroxyphenylketocumaran* previously suggested (*loc. cit.*) for genistein. Genistein from *Genista tinctoria* melts at 291–293°.

142. "The Colouring Matter of the Flowers of *Delphinium consolida*." By A. G. PERKIN and E. J. WILKINSON. The presence of a yellow colouring matter in these flowers (in the form of glucoside) has been previously notified (*Trans.*, 1898, lxxiii., 275). This compound forms yellow needles, has the composition $C_{15}H_{10}O_6$ (found C=62.85; H=3.63 per cent), and on fusion with alkali gives phloroglucinol and *p*-hydroxybenzoic acid (found C=60.71; H=3.94). The *tetracetyl* compound, $C_{15}H_6O_6(C_2H_3O)_4$ (found C=60.64; H=4.17), is peculiar, for when crystallised from alcohol it melts at about 114–116°, re-solidifies at a higher temperature, and again melts at 181–183°. This is not due to alcohol of crystallisation. The sulphate, $C_{15}H_{10}O_6.H_2SO_4$, orange-red needles (found C=46.71; H=3.39, the *hydriodide*, $C_{15}H_{10}O_6HI$ (found C=44.25; H=3.00, and the *monopotassium salt*, $C_{15}H_9O_6K$ (found K=11.85), have been obtained, but are less stable than is usually the case with such compounds. The colouring matter has properties resembling those assigned to kampherol (Gordin, *Diss. Berne*, 1897), obtained by the decomposition of its methyl ether, kampherid, which exists in galanga root (*Alpinia officinarum*). The investigation will be continued with the hope of ascertaining the identity of this colouring matter with certainty.

143. "Note on Gallinek's Amidomethylnaphthimidazole." By RAPHAEL MELDOLA, F.R.S., and FREDERICK WILLIAM STREATFEILD.

A paper by Gallinek has just been published (*Ber.*, 1900, xxxiii., 2315) on a sulphonic acid of the anhydro-base obtained by reducing dinitro-*a*-acetnaphthalide. Gallinek assumes that the base he has been dealing with is the same as that described by the authors (*Trans.*, 1887, li., 69x, and he considers that their failure to separate the base in the free state was due to their having had impure dinitro-*a*-acetnaphthalide as their raw material. The authors desire to point out that Gallinek is completely in error in his original assumption, and that the base described by him is isomeric, and not identical with that described by the authors in 1887. Gallinek does not state what reducing agent he employed, nor does he refer to the process published by Markfeldt (*Ber.*, 1898, xxxi., 1174), but his description of the base as being stable, solid, and crystallisable from water, renders it tolerably certain that he has been investigating Markfeldt's base. Markfeldt also assumed that his base was identical with that described by the authors in 1887. The isomerism was recently made known, and the properties of the base obtained by Markfeldt's process somewhat fully characterised (Meldola and Eynon, *Trans.*, 1900, lxxvii., 1159). The authors think it necessary to indicate the true cause of the apparent discrepancy between the statements of the German investigators and themselves, because they are at present engaged in the further investigation of the nature of the isomerism.

144. "The Amount of Chlorine in Rain Water collected at Cirencester." By EDWARD KINCH.

The author has already published the results (*Trans.*, 1887, li., 92) of the estimation of the chlorine in the water collected in a rain-gauge at the Royal Agricultural College, 443 feet above sea-level, and about 35 miles distant from the sea. The results of his determinations up to the present time are summarised in the table.

The rain-water for periods of six months, namely, summer months, April to September, and winter months, October to March, inclusive, gave the averages shown in the accompanying table.

145. "Researches on the Alkyl-substituted Succinic Acids III. Dissociation Constants." By W. A. BONE and C. H. G. SPANKLING.

The authors have prepared, and determined the dissociation constants of, a number of new alkyl-substituted succinic acids as follows:—

		M. p.	K.
sym Di-isobutylsuccinic ..	<i>trans</i> ..	195°	0.0225
	<i>cis</i> ..	97–98	0.056
aa ₁ -Methylpropylsuccinic ..	<i>trans</i> ..	158–160	0.0355
	<i>cis</i> ..	92–93	0.0271
aa ₁ -Methylisobutylsuccinic ..	<i>trans</i> ..	133	0.0427
	<i>cis</i> ..	88–90	0.0236
aa ₁ -Methylisoamylsuccinic ..	<i>trans</i> ..	141–142	0.0236
	<i>cis</i> ..	93	0.0385
aa-Dimethyl- <i>a</i> ₁ -ethylsuccinic ..	..	139–140	0.0566
aa-Dimethyl- <i>a</i> ₁ -propylsuccinic ..	..	145	0.060
aa-Dimethyl- <i>a</i> ₁ -isopropylsuccinic ..	..	141–142	0.0158
aa-Dimethyl- <i>a</i> ₁ -isobutylsuccinic ..	..	143–144	0.0432
aa-Dimethyl- <i>a</i> ₁ -isoamylsuccinic ..	..	143–144	0.0616

They then discuss, in the light of the above and previous results, the effect of alkyl-substitution on the magnitude of the dissociation-constant of a succinic acid, and deduce the following conclusions:—

Each alkyl group exerts its own influence upon the constant dependent on its mass and structure. In the case of normal radicles, where the influence of "mass" only is to be traced, an increase in the mass of the alkyl is invariably accompanied by a corresponding rise in the constant. In the case of "iso"-radicles there is, however, a "structural" effect opposed to that of mass, except in the case of the *cis* aa₁-substituted acids, which are separately discussed: the magnitude of this structural effect is always dependent on the proximity of the "iso"-linkage to the carbon atom to which the carboxyl group is attached.

146. "The Reaction between Ethyl Alcohol and Hydrochloric Acid." By T. SLATER PRICE, D.Sc.

The present investigation was undertaken in order to measure the velocity of reaction between hydrochloric acid and ethyl alcohol. On re-determining the equilibrium constants it was found that they varied with the amount of acid used. The constants (*a*) were calculated according to the equation $a = (A-x)(B-x)/(C+x)(D+x)$, where A, B, C, and D are the concentrations of the alcohol, acid, water, and ester respectively at the commencement of the reaction, and *x* the amount of fresh ester formed when equilibrium is reached. The results obtained agree with those of Zaitseck (*Zeit. Phys. Chem.*, 1897, xxiv., 1), who investigated the action of sulphuric acid on alcohol.

Determinations were made at 77°, 99°, and 129.5°. The value of *a* decreases as the amount of acid increases: this is well shown especially in the experiments at 77°, as the lower the temperature the greater is the variation.

Periods.	Rainfall in inches.	Chlorine per million.	Equivalent to NaCl, grms. per gallon.	Equivalent to NaCl, lbs. per acre.
Mean of 14 winter periods to March, 1900 ..	14.26	3.55	0.412	19.35
Mean of 14 summer periods to September, 1900 ..	12.78	2.27	0.261	10.40
Average of 14 years to September, 1900 ..	27.04	2.91	0.337	29.75
Mean of 26 winter periods to March, 1900 ..	15.83	3.76	0.435	21.29
Mean of 26 summer periods to September, 1900 ..	14.78	2.58	0.302	14.81
Average of 26 years to September 31st, 1900 ..	30.61	3.17	0.369	36.10

The results obtained by the author are found to agree very well with the equation—

$$dx/d\theta = k_1(A-x)(B-x)^a - k_2(C+x)(D+x)(B-x),$$

k_1 and k_2 are the velocity constants of the direct and reverse reactions, x is the amount of ester formed after the time θ , and A, B, C, and D have the signification given above. The catalytic effect of the hydrogen ions is assumed to be proportional to the amount $(B-x)$ of acid present, this holding good over a short interval of time, and since both the direct and reverse reactions are affected the factor $(B-x)$ will be extra in each term of the velocity equation. The values of k_1 so obtained, are especially good when no water is present to begin with, that is, when $C=0$ (in no case was ester present at the commencement of the reaction), but when the reaction mixture used contained water to start with, the values of k_1 diminish as θ increases.

The value of k_1 decreases as the concentration of the acid increases, and is also greatly diminished when water is present.

The velocity of reaction increases very rapidly with the temperature, the increase being much greater than in the case of the action of organic acids on alcohol.

PHYSICAL SOCIETY.

Ordinary Meeting, November 23rd, 1900.

Prof. EVERETT, F.R.S., Vice-President, in the Chair.

A PAPER ON "A Self-adjusting Wheatstone's Bridge," by E. H. GRIFFITHS and W. C. D. WHETHAM, was read by Mr. WHETHAM.

The object of this paper is to describe a cheap and easy method of getting a self-adjusting bridge to show on a scale the actual resistance of any wire. Contact with the bridge-wire is made by means of a light horizontal bar which is suspended by a phosphor-bronze strip from the coil of the d'Arsonval galvanometer used with the instrument. A second bar, parallel to and above the first, is rigidly connected with the coil. A wooden beam, worked by clockwork, moves up and down between the bars, and clamps them alternately. When the beam is down, contact is made with the bridge-wire. If this contact is not at the zero-point, a current will flow through the coil, and, if the cell is connected up the proper way, it will turn the coil so as to bring the upper bar nearer to the null-point; this puts a twist into the phosphor-bronze strip, and when the beam rises and clamps the upper bar, the torsion comes into play and brings the lower bar under the upper one; the beam then descends and makes contact at this point, and if any current flows through the galvanometer, there is further movement until the null-point is reached. Any alteration in the resistance of the wire under experiment causes a movement of the zero-point on the bridge-wire, and this is followed by the lower arm. The position of the lower arm can be directly indicated by means of a scale.

Prof. S. P. THOMPSON asked how the scale was calibrated.

Mr. WHETHAM said the scale was arbitrary, but it could be calibrated by the known resistance of the bridge-wire per unit length. Extension of the range can be obtained by shunting the bridge-wire with various resistances.

Mr. GLAZEBROOK asked how sensitive the bridge was.

Mr. WHETHAM said that, working with a dry cell, it could easily indicate 1Ω on a platinum thermometer.

Mr. BLAKESLEY pointed out that if the cell was connected up the wrong way, the zero-point would be an unstable one.

A paper on "The Liquefaction of Hydrogen" was read by Dr. M. W. TRAVERS.

These experiments were undertaken in order to provide liquid hydrogen in sufficient quantity for the separation of neon from the helium with which it is usually mixed. The separation is effected by cooling the gases to the temperature of hydrogen boiling at atmospheric pressure.

The principles and conclusions do not differ from those of Dewar, but as the production of liquid hydrogen is neither difficult or costly, an account of the experiments is given.

In 1884, Wroblewski showed that strongly cooled and compressed hydrogen on being allowed to expand formed mist or spray in the tube; and, later, Olszewski repeated these experiments on a larger scale, and determined the temperature of the liquid. Other methods of liquefying hydrogen have been suggested by Lord Rayleigh and Kammerlingh Onnes. In the case of many gases a fall of temperature takes place on free expansion, but under ordinary circumstances the temperature rises in the case of hydrogen and helium. The principle of free expansion was first applied by Hampson and Linde to the liquefaction of air. Within the last two years, Dewar has shown that at a temperature close to -200°C , hydrogen behaves as an imperfect gas, and becomes cooled when allowed to expand. This principle has been applied by Dewar to the liquefaction of hydrogen in quantity. In the author's experiments, hydrogen under a pressure of 200 atmospheres passes through a coil which is cooled to -80°C . by a mixture of solid carbonic acid and alcohol. It then enters another coil contained in a chamber which is continually replenished with liquid air. The lower portion of this coil passes into another chamber, which is closed and communicates through a pipe with an exhaust pump. Liquid air flows continuously from the first chamber into the second through a pin valve controlled by a lever. The liquid air, boiling under a pressure of 100 m.m. of mercury, lowers the temperature to -200°C . The gas then passes into a regenerator coil, which is enclosed in a vacuum vessel, and, expanding at a valve, passes upwards, through the interstices of the coil and the annular space surrounding the chambers through which the gas first passes, to an outlet whence it can return to the main supply pipe. The liquid which separates from the gas is ultimately collected in a vacuum vessel.

The apparatus, with the exception of the compressor, motor, and Hampson air liquefier, is comparatively inexpensive. About £50 is required for the additional apparatus, and each time liquid hydrogen is made involves a further expenditure of about a sovereign.

Dr. HAMPSON said he would like to offer a correction. Dr. Travers had said that he (Dr. Hampson) was the first to liquify air by the application of the counter current process to the Joule-Thomson effect. Although he was the first to make the proposal, he was not the first to apply it. He made the proposal to Prof. Dewar's assistant in 1894, and air was liquefied by Prof. Dewar by this method. Dr. Travers had referred at length to a valve which he (Dr. Hampson) had devised, but as it was straightforward common sense he did not wish to accept any credit for the use it had been to the author in his experiments. He would like to call attention to the remarkable features of the work in two respects:—The economy of means and the magnitude of results. By means of liquid hydrogen Prof. Ramsay and Dr. Travers had succeeded in obtaining the physical and other properties of some of the rarer gases.

Prof. S. P. THOMPSON said the author had asserted that the Joule-Thomson effect for hydrogen changes in sign at some temperatures, and expressed his interest in the fact that it was possible to get a cooling effect by allowing hydrogen to expand.

Mr. BOYS asked if it was necessary or desirable to allow the hydrogen to expand to atmospheric pressure.

Dr. TRAVERS said the mechanical advantages of this were great.

Dr. LEHFELDT asked if there had been any attempt to determine the temperature of the liquid, and, secondly, if the apparatus could be employed to determine the magnitude of the Joule-Thomson effect.

Dr. HARKER asked if the temperature at which the Joule-Thomson effect changes sign was known.

Dr. DONNAN said that the effect changed sign at the temperature at which " p_v " was a minimum.

Dr. TRAVERS, in reply to Dr. Lehfeldt, said he had not

determined the temperature of the liquid, and the apparatus was not suitable for measuring the Joule-Thomson effect. He should say that the change of sign occurred about -150°C . It was Daniel Berthelot who first pointed out that the change of sign corresponded with the minimum value of " ρv ," but the experiments of Amagat on the relation between pressure and volume were not sufficiently accurate to fix the temperature.

A paper on "*The Anomalous Dispersion of Carbon*," by Prof. R. W. Wood, was taken as read.

Experiments were made with smoke-films, and with films deposited on plate-glass in a vacuum by an incandescent lamp. The dispersion was first measured with a Michelson interferometer, illuminated with monochromatic light of various colours obtained by prismatic analysis. The fringes were photographed and measured, readings being obtained between wave lengths 0.000040 c.m. and 0.000066 c.m. The results show a steady increase of refractive index from blue to red. The refractive index for sodium light was measured by estimating the thickness of the film and the fringe displacement, and was found to be 2.2. A prismatic deposit of smoke was then made by allowing a piece of plate-glass to move uniformly backwards and forwards over the top of a small flame. The deviation produced by this prism was measured by means of a direct vision spectroscopy, with the prisms removed. Experiments were performed with red and blue light. The mean deviation of red and blue was taken for sodium light, and this result was in good agreement with the deviation obtained by the interferometer method.

A paper on "*The Refraction of Sound by Wind*," by Dr. E. H. BARTON, was taken as read.

Assuming that the wind is everywhere horizontal, and does not vary in any one horizontal plane, but is different at different levels, then the following results are obtained for rays in the same vertical plane as the wind:—1. The direction of propagation is not usually at right angles to the wave-front where there is a wind; consequently, the cosecant law for the wave-front needs supplementing by another expression giving the direction of the ray. 2. Total reflection cannot occur if the wave-front is initially horizontal. 3. In a region where the horizontal wind increases uniformly as we ascend, the rays instead of forming a catenary describe a more complicated curve, which, however, reduces to a parabola in the special case of rays whose wave-fronts are horizontal. In the paper the relation between direction of propagation and wave-front is first worked out, and then the refraction of waves and rays on crossing into a new wind-zone is considered. This principle is then applied to the diffraction through any number of parallel wind-zones, and it is shown that the final inclinations of wave-fronts and rays are independent of the characteristic constants of the intermediate zones. It is shown that since a cosecant cannot have a value between $+1$ and -1 , total reflection becomes possible. If, however, the wave-front is initially horizontal there is no refraction of the wave-front, and no total reflection; but the ray deviates without limit from the vertical, and tends to correspond with the wave-front. When reflexion occurs it follows the ordinary optical law.

The Society then adjourned until December 14th, when the meeting will be held at the Royal College of Science, South Kensington.

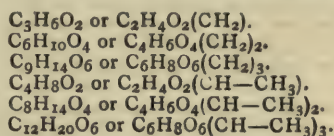
Simultaneous presence of Saccharose and Gentianose in the Fresh Root of Gentian.—E. Bourquelot and H. Hérissay.—The simultaneous presence of gentianose and saccharose in the same vegetable organism has not been found before. The author, from a study of previous experiments on gentianose, a sugar whose exact constitution has not yet been fixed, believes that the cane-sugar which is found in the fresh root of the gentian is produced by a peculiar splitting-up of the gentianose itself.—*Comptes Rendus*, cxxxi., No. 19.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 19, November 5, 1900.

Acetals of Plurivalent Alcohols.—Marcel Delépine.—The author determines the heats of combustion and formation of the glycol formals and acetals having formulae—



The formals of these three poly-alcohols, besides the acetals of glycol and of mannite, are known already, but the author prepares them by a new and easy method. The numbers obtained by him show that, in the same way as the monovalent alcohol acetals, the formation of plurivalent alcohol acetals is also a limited reaction.

Constitution of Nitrated Derivatives of Ethyl Dimethylacrylate: Ethyl Nitroacetate.—L. Bouveault and A. Wahl.—In a former paper the authors showed that fuming nitric acid transforms ethyl dimethylacrylate into a substance possessing the composition of its nitrated derivative. This compound does not dissolve in dilute cold alkalis, but alcoholic potash transforms it into the potassium salt, of a different nitrated derivative, this latter being the isomer of the first and soluble in dilute alkalis. The first the author calls α - and the second β -dimethylacrylate of ethyl. These two substances are different in that the second alone contains a negative atom of hydrogen, capable of being replaced by potassium. There actually exist two nitroacetic ethers having equal rights to the name. The authors contend that their α -nitro-methylacrylic ether, but not its β isomer, is split up by hydration into acetone and nitroacetic ether. They show that the group NO_2 is in the molecule united with carbon, and directly to the same atom of carbon which holds also the group $\text{CO}_2\text{C}_2\text{H}_5$.

A New Glucoside extracted from the Seeds of Erysimum, of the Crucifer Family.—MM. Schlagdenhauffen and Reeb.—The authors' experiments show that the seeds of *Erysimum aureum*, an ornamental garden plant, contain two active principles—one of an alkaloidal nature which provokes paralysis, and the other a glucoside, which constitutes a violent poison, affecting the heart.

MISCELLANEOUS.

The Vapour-density of Sulphur.—O. Bleier and L. Kohn.—The authors have measured the vapour-density of sulphur at reduced pressure, and arrive at the conclusion that the lower the temperature the more the condensation of the molecule of sulphur approaches S_8 , as shown by the following table:—

Temperature.	Pressure. M.m.	Density of the vapour with regard to oxygen.
Boiling-point of—		
Diphenylamine, 310° ..	42.6	7.44
Benzoate of amyl, 262° ..	15.0	7.50
Quinoline, 236° ..	9.4	7.66
Benzoate of ethyl, 212° ..	4.2	7.80
Dimethylaniline, 193° ..	2.1	7.85

—*Berichte*, xxxiii., p. 50.

Society of Arts.—The Juvenile Lectures at the Society of Arts will be given this Session on the afternoons of Wednesday, January 2 and 9, by Mr. E. Walter Maunder, F.R.A.S., Superintendent of the Solar Department, Greenwich Observatory. The subject of the course will be "Eclipses."

MEETINGS FOR THE WEEK.

MONDAY, Dec. 3rd.—Royal Institution, 5. General Monthly Meeting.
TUESDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Electric Oscillations and Electric Waves," by Prof. John A. Fleming, M.A., D.Sc., F.R.S.

WEDNESDAY, 5th.—Society of Arts, 8. "Road Traction," by Prof. H. S. Hele-Shaw, LL.D., F.R.S.

THURSDAY, 6th.—Chemical, 8. Ballot for the election of Fellows. "Santalénic Acid," by Alfred C. Chapman. "Ammonium Bromide and the Atomic Weight of Nitrogen," by A. Scott, F.R.S. "Interaction between Urethanes and Primary Benzenoid Amines," by A. E. Dixon, M.D. "The Decomposition of Chlorates—Part III., Calcium Chlorate and Silver Chlorate," by W. H. Sodeau, B.Sc. "Nitride of Iron," by Gilbert J. Fowler, M.Sc. "The Heat of Formation and Constitution of Iron Nitride," by Gilbert J. Fowler, M.Sc., and Philip J. Hartog, B.Sc. "Relationships of Oxalacetic Acid," by H. J. H. Fenton, F.R.S., and H. O. Jones, B.A., B.Sc.

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MICHAELMAS TERM.—Monday, October 1, to Saturday December 15.

LENT TERM.—Monday, January 7, to Saturday, March 30.

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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2141.

THE ANALYSIS OF FERRO-SILICON AND SILICO-SPIEGEL.

By FRED. IBBOTSON and HARRY BREARLEY.

Total Carbon.

THE powdered alloys are hardly at all attacked by cold, and only partially by hot copper solutions, but they are easily and completely decarbonised by ignition in a stream of oxygen, either with or without such oxidising reagents as copper oxide and lead chromate. Better without, because there is then no reagent blank to be determined and allowed for, and there are no metallic beads (Cu or Pb) formed which may occlude some of the unattacked sample. As there is generally no fusion, the same boat is available time after time. The ferro-silicon after ignition is powdery or easily crumbled; silico-spiegel is fritted into a single cake.

Graphite.

The carbon in ferro-silicon exists chiefly as graphite, the combined carbon rarely amounting to more than a few tenths per cent.

	Londsdale.	Ayresome.	Mostyn.
Combined C	0.20	0.15	0.19
Graphite	1.39	1.39	1.62
Silicon	12.32	13.28	12.08

The graphite is determined as follows, combined carbon being obtained by difference:—Cover 2 or 3 grms. of the powdered alloy with 70 to 100 c.c. of nitric acid (1.20), and heat nearly to boiling; the reaction with ferro-silicon is very slight. Add a few drops of hydrofluoric acid; the reaction becomes very vigorous. Keep up the reaction by adding small amounts of hydrofluoric acid until only particles of graphite are to be seen. Do not hurry the reaction; give the flocks of the nitrated (combined) carbon compound time to dissolve in the nitric acid before any considerable excess of hydrofluoric acid is added. The sample may be dissolved in glass vessels without injuring them; they are preferable to platinum ware, in that they permit the course of the reaction and the complete decomposition to be readily observed. Filter the graphite on to asbestos, wash first with water, and then with boiling soda hydrate in order to dissolve out any carbonaceous matter not graphite, wash once with dilute hydrochloric acid, and finally with water until the washings are free from chlorine. Burn in a current of oxygen, in the usual way.

Donath and Hallsig (*Stahl und Eisen*, xvii., 670, and *Z. I. S. I.*, 1897, ii., 488) examined a ferro-silicon which contained 14.3 per cent silicon and as much as 1.39 per cent combined carbon, which the authors believe was present in the alloy as carbide of silicon (carborundum). In the process given below for estimating silicon, carborundum, if present, would be with the silica, and after treatment with hydrofluoric acid would still be in the residue undecomposed. This residue, however, in our experience, never exceeds 2 or 3 m.grms., and consists chiefly of ferric oxide; so that generally the existence of carbide of silicon in ferro-silicon, for other reasons as well as that just given, is very unlikely.

The total carbon of silico-spiegel is generally higher than that of ferro-silicon, and contains more combined carbon. The graphite and combined carbon are estimated as above. Some examples are:—

	I.	II.	III.	IV.
Combined C. ..	1.89	1.61	1.31	0.51
Graphite	0.34	0.94	0.60	1.22
Silicon	10.53	10.95	12.10	13.34
Manganese ..	19.85	18.14	18.25	20.20

Silicon.

The statement that these alloys cannot be completely decomposed by any mixture of the acids, but must be attacked by fusion with KHSO_4 , Na_2CO_3 , or Na_2O_2 , is erroneous. They are very readily attacked by a mixture of nitric and hydrochloric acids.

Hogg (*CHEM. NEWS*, lxxvii., 27) points out that, after evaporation of the acid liquid and treatment of the residue with hydrochloric acid, the silica is always discoloured, not because the alloy has been incompletely decomposed, but because the physical condition of the silica is so peculiar that when heated with an iron salt, in the dry state, it takes up and firmly retains some ferric oxide. Hogg also shows that for alloys containing from 10 to 15 per cent of silicon the amount of Si which goes into solution lies between 0.1 and 0.3 per cent: this amount he omits to recover, and adds, by way of correction, 0.2 per cent to that obtained by filtering as soon as the decomposition is completed. A large number of test analyses enable us to confirm Hogg's conclusions in every particular, save the minor one referred to in the following account of the process:—

Weigh off 2 grms. of the finely-powdered alloy, add 50 c.c. concentrated HCl and 10 to 20 c.c. HNO_3 ; boil to decomposition, which needs 10 to 15 minutes; add about twice the volume of water and filter *at once*, wash with dilute HCl, ignite, and weigh. To the result obtained add only 0.1 per cent as a correction for the soluble silica.

The amount of silicon which goes into solution is increased by boiling the solution after diluting.* By allowing the diluted solution to stand on the hot plate for two hours, between 20 and 30 m.grms. SiO_2 were dissolved; the correction, therefore, of 0.1 per cent applies only when the filtration is proceeded with immediately after diluting. The silica as weighed is in a very fine state of division, and is also very hygroscopic.

Manganese.

The alloys are most readily decomposed by nitrofluoric acid. In ferro-silicon the manganese is often so low that it can be estimated by oxidising with red-lead and titrating the permanganic acid with FeSO_4 , &c. Not more than 0.07 grm. Mn can, however, be assayed by this process.

Reddrop and Ramage (*Journ. Chem. Soc.*, lxxvii., 268) use soda bismuthate in cold solutions, in order to convert manganous oxide to permanganate. This process works as well for large as for small amounts of manganese:—Dissolve 1 grm. of the alloy in 30 c.c. 1.20 HNO_3 and 1 or 2 c.c. HF; make quite cold, add 10 c.c. water, and then add about 2 grms. of soda bismuthate. Filter through asbestos, add standard H_2O_2 , and titrate with N/10 permanganate. For silico-spiegels dilute the dissolved alloy to 100 c.c., measure out 25 c.c., add 25 c.c. 1.20 HNO_3 , oxidise as before, filter into H_2O_2 ,† and titrate the excess with KMnO_4 . For a full description of the process the original paper must be referred to, the present object being merely to note that silicon alloys are most conveniently prepared for the estimation of the manganese by decomposing with fluor-nitric acid, and that the use of hydrofluoric acid does not interfere with any phase of the bismuthate process. Needless large amounts of HF, however, may cause the final permanganate tint to be readily converted, through the agency of manganous fluoride, into manganic oxide.

* A. H. Allen has shown that when irons are attacked with HCl or H_2SO_4 , part of the silicon is liberated as "leucon," which is soluble in dilute acids.

† Reddrop and Ramage offer no reason why, for steels and low manganiferous alloys, the hydrogen peroxide is added to the permanganate and for spieglers and highly manganiferous alloys the permanganate is filtered into the peroxide. The distinction is a necessary one; can it be explained?

Phosphorus.

We have described a process for estimating phosphorus (CHEM. NEWS, lxxxii., 55) depending on the conversion of the Mo in the $\text{Am}_2\text{PO}_4\cdot 12\text{MoO}_3$ into PbMoO_4 , but it cannot be straightaway applied to these alloys, because neither of them are decomposed by 1·20 nitric acid.

By decomposing with nitro-hydrochloric acid, and evaporating so as to dehydrate the silica and eliminate HCl, a portion of the P always remains with the SiO_2 . This may be a source of very serious error when highly phosphoretted material is being assayed. As an example we may quote a silico-spiegel, where of the 0·20 per cent P present 0·063 per cent was found with the ignited silica. An obvious means of minimising, if not altogether eliminating this error, is to filter as soon as the sample is decomposed, as in the estimation of silicon, and use the evaporated filtrate for the estimation of phosphorus.

A more expeditious way of estimating the phosphorus is suggested by the easy decomposition of these silicon alloys with nitrofluoric acid. To decompose the silica in the solution would at once allay all fear of P being filtered off. But the precipitation of P as ammonium phospho-molybdate is by no means insensible to the presence of hydrofluoric acid. A number of experiments made with dilute solutions of soda phosphate showed that small amounts of HF retarded the precipitation of the phospho-molybdate, and larger amounts altogether prevented it. Much the same thing happens when the nitric acid solution of a steel from which P is to be precipitated is treated with hydrofluoric acid.

By preparing identical solutions of the same steel which contained 0·064 per cent of phosphorus, and adding 1·7, 3·4, and 5·1 c.c. hydrofluoric acid just before adding the Am_2MoO_4 reagent, we found the first to be precipitated at once, but the second and third to show no signs of a precipitate for some time. After standing for two hours at about 60° the filtered precipitates were converted to PbMoO_4 , and found to correspond to 0·060, 0·063, and 0·061 per cent phosphorus.

Along with the usual amount of nitric acid, a ferro-silicon or silico-spiegel can be easily decomposed by using 4 c.c., or less, of hydrofluoric acid; what portion of this is unused by the silicon of the alloy is largely eliminated by the subsequent boilings, so that a series of tests made by adding pure silica to the steel being dissolved by nitrofluoric showed no signs, when the phosphorus came to be precipitated, that any hydrofluoric acid had been used, and, on completing the estimations, gave 0·065, 0·063, 0·064, and 0·066, instead of the 0·064 per cent P actually present. It is clear then that hydrofluoric acid may be safely used. The process is most conveniently carried out as follows:—

To 2 grms. of the powdered alloy add 45 c.c. 1·20 nitric acid, and 25 to 30 drops hydrofluoric acid. When, without the application of heat, the reaction subsides, add another 25 to 30 drops HF. What little of the alloy is then decomposed goes on boiling. After complete decomposition add permanganate until a permanent MnO_2 precipitate is formed, clear with FeSO_4 , filter off the graphite, add 6 or 7 c.c. strong ammonia, precipitate with Am_2MoO_4 reagent, and weigh finally as PbMoO_4 as described in our previous paper.

Hydrofluoric acid may contain small amounts of phosphoric acid. It is estimated (and allowed for) by evaporating 100 or 200 drops of the acid with sulphuric acid in a platinum dish until SO_3 fumes are given off, transferring to a glass vessel, oxidising with permanganate, clearing with FeSO_4 , adding AmHO to precipitation of Fe, re-dissolving in HNO_3 , precipitating with Am_2MoO_4 mixture, and finishing as usual.

We have never found ten times as much permanganate and ferrous sulphate as are used for each assay to contain an appreciable amount of phosphorus.

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SCHÖFFEL'S PROCESS FOR ESTIMATING
TUNGSTEN IN STEEL.

By ERNEST BAGLEY and HARRY BREARLEY.

SCHÖFFEL'S process for estimating tungsten in steel does not meet with anything like the practical appreciation it deserves if we may take the processes commonly described in text-books as indicating the practice of works' laboratories.

The process (CHEMICAL NEWS, xli., 31) depends on the fact that a neutral solution of a double copper salt, such as is often used for liberating carbon from iron, leaves all the tungsten unattacked. After ignition of the carbonaceous residue and removal of the silica, the solution of the fused tungstic oxide is precipitated with mercurous nitrate.

Besides carbon, tungsten, and silicon, the residue will also contain sulphur, associated with iron and manganese; chromium, together with considerable iron; titanium, when it happens to be present in the steel; and, if the copper solution is quite neutral, all the phosphorus.

Sulphur and phosphorus are usually present in such small amounts that no appreciable error could be introduced by volatilising the silica with hydrofluoric acid, fusing the residue with soda carbonate, filtering off and weighing the small amount of iron or manganese, and arriving at the percentage of tungsten by difference. Such a procedure gives quite accurate results when applied to steels in which tungsten only is the uncommon element. But in case chromium were present, the iron to be filtered off after the soda carbonate fusion would be a large amount, and the chromium would pass, partly at least, into solution. Under such unfavourable circumstances, if the operations are carefully performed, very tolerable results are obtainable by titrating the chromic acid in the acidified filtrate, adding its Cr_2O_3 equivalent to the mixture of $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ which has been filtered off and ignited, and deducting the total from the weight before fusion, so as to arrive at the amount of tungstic oxide.

It may occasionally or even frequently happen that the tungstic oxide found by difference in the above manner is less than the amount of impurities associated with it; and in this fact, at a time when chromium and tungsten are so often associated in steels, lies the weakness of Schöffel's process for general purposes.

By decomposing chrome-tungsten steels with cupric solutions which are made increasingly acid with HCl, the amount of impurity to be found in the ignited carbonaceous residue becomes less and less. By using solutions which contained one-third their volume of strong hydrochloric acid, we have obtained such residues as contain no very objectionable amount of either iron or chromium and all the tungsten.

Weigh off 5 grms. of the sample, add 50 grms. cuprammonium chloride crystals, 100 c.c. hot water, and 50 c.c. strong hydrochloric acid. By digesting at boiling-point, with occasional shaking, the precipitated copper dissolves in half an hour or so, and after standing a little longer, the solution is filtered through paper pulp. Wash with dilute HCl, ignite, volatilise silica with HF, fuse with Na_2CO_3 , dissolve in water, and ignite the separated Fe_2O_3 , &c. The filtrate may have a faint yellow colour; if so, acidify with H_2SO_4 , add FeSO_4 , titrate with KMnO_4 , calculate to Cr_2O_3 , and deduct along with the Fe_2O_3 in order to arrive at the percentage of tungsten.

That all the tungsten remains with the residue when strongly acid copper solutions are used, is shown by the following analyses:—

Percentage tungsten by—

Evaporating with acids or other standard process.	Digesting with 33 per cent HCl cuprammonium chloride.
4·50	4·52
10·06	10·09
3·41	3·44
1·62	1·62

And the amount of impurity ($\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$), of which account has to be taken, may be seen from the following:—

Percentage tungsten.		Percentage Cr present.	Weight in the residue of—	
Standard process.	33 per cent HCl.Cu.		Cr_2O_3 .	Fe_2O_3 .
8.81	8.81	2.25	0.0020	0.0100
6.28	6.33	0.80	trace	0.0060
—	3.32	2.51	0.0008	0.0050
3.43	3.40	1.44	trace	0.0050

When steels which contain both tungsten and molybdenum are treated in this way, the molybdenum may go wholly into solution on continued digestion, but this is not invariably the case.

When the tungsten is but a fraction of 1 per cent, the treatment at boiling-point with solutions containing one-third their volume of strong hydrochloric acid causes the results to be slightly low. In such cases treatment of the steel with cuprammonium solutions containing only 10 per cent of strong hydrochloric acid is preferable.

Part of the silicon passes into solution, and cannot therefore be estimated by measuring the loss in weight on treating with hydrofluoric acid.

SOME RESULTS OBTAINED IN THE ELECTROLYSIS OF FUSED SALTS.

By F. MAXWELL LYTE.

A PATENT of the writer's for the electrolysis of fused lead chloride was being experimented on by Mr. O. J. Steinhart (Chemist to the Chemical and Electrolytic Syndicate), which company had taken over several of the writer's patents with the object of working them. These experiments were made on about 5 or 6 lbs. of lead chloride at a time.

The lead chloride, after being well dried, was fused in an earthen pot, into which another rather smaller, but similar vessel, was inverted, forming a sort of bell with its lower part dipping into the molten chloride. Two carbon rods intended to serve as cathode and anode were cemented gas-tight into the top of the bell, with a cement composed of sodium silicate and china clay, with their lower ends dipping an inch or two into the fused lead chloride. A peep-hole was also arranged in the top of the bell so as to be able to look down into it and see what passed.

The writer himself was unable to be present owing to illness, but his son, Mr. C. Maxwell Lyte, though neither a chemist nor an electrician, was able to report all that occurred with so much clearness and exactitude, that the writer almost felt as if he himself had assisted at the operations.

On passing the electric current at a pressure sufficient to cause the electrolysis of the fused lead chloride, a strange phenomenon presented itself. The space between the electrodes at once became occupied by what these gentlemen characterised as a kind of smoke or cloud, emanating apparently from the immediate neighbourhood of the cathode, and growing less and less intense as it approached the anode, in the vicinity of which it apparently disappeared altogether.

During the whole experiment little or no chlorine was obtained, only a small amount of a colourless and odourless gas, which later on was found to be oxygen, being evolved from the anode, while from time to time a little metallic lead was seen to drip from the cathode.

All or most of this lead was probably derived from the decomposition of the lead oxide in the lead oxychloride, formed in the fused lead chloride, which dissolves it, by the absorption of atmospheric oxygen. Lead and oxygen have a lower heat of combination than lead and chlorine, and consequently the lead oxide would decompose first,

casting about in order to find some means of preventing this reaction, and of avoiding the re-combination of the lead with the chlorine which evidently occurred, and which obviously would result in a considerable loss, the writer came to the conclusion, which seemed almost self-evident, that if instead of using a carbon cathode, the fused metal itself were made the cathode, the lead resulting from the electrolysis would be no longer diffused into the electrolyte, but would be deposited on and amalgamated with the fused lead cathode, and that thus the so-called cloud or smoke no longer being formed, that cause of loss would disappear.

This we at once tried, and it resulted apparently in a complete success, but when afterwards the experiment was tried quantitatively, it was found that there was still a loss of about 10 per cent of the chlorine that should theoretically be produced. This may have arisen from an absorption of oxygen, as already mentioned, or from leakage, but nevertheless it would be found difficult in practice to avoid all loss. The matter formed the subject of two successive patents by the writer, one for the electrolysis of fused lead chloride with a carbon anode and a fused lead cathode, No. 7264, April 8, 1893, and later on another for the electrolysis of fused zinc chloride with the same arrangement of the electrodes, No. 15,813, August 22, 1895.

The lead chloride patent was ultimately abandoned for various reasons, notably, among others, from the difficulty of obtaining the lead chloride on the large scale with sufficient ease and economy.

Zinc chloride, on the other hand, can be easily produced from the ore or from the zinc oxide resulting from its treatment, and the zinc chloride patent offers besides this several other advantages.

The process has lately undergone a very long and exhausting trial on a large scale, and is soon now about to be worked for manufacturing purposes.

The above-mentioned smoke or cloud of metallic lead, forming between the electrodes and disappearing as it approached the carbon anode, affords a ready explanation of the insurmountable difficulties which seem to attend all attempts of the electrolysis of aqueous solutions of the salts of the more readily oxidisable metals, such as potassium, sodium, zinc, &c., where a solid cathode is employed, zinc when in the nascent or finely divided state decomposing water with peculiar facility.

The analysis of the black deposit resulting from the electrolysis of aqueous solutions of zinc salts has shown it to be a mixture of metallic zinc and zinc oxide, just such as we might expect to find with a metal the heat units evolved by which in its combination with oxygen so nearly corresponded with those evolved by hydrogen in like circumstances.

The writer would not now allude to the above-mentioned experiments, which date from some seven or eight years back, and which were thought hardly worth publication at the time, they not seeming in themselves to have sufficient scientific interest, and he would simply have contented himself with having obtained the two patents above mentioned, had not the subject again cropped up lately in the experiments of A. Helfenstein, related in the number for July, 1900, of the *Journ. Chem. Soc. (Abstracts, Part II., p. 383)*. He seems to have operated in an ordinary V-tube, and not on nearly so large a scale as we did, using a fused lead cathode. Consequently, he did not get the cloud of metallic lead which we did when working with a carbon cathode.

In Faraday's account of his own experiments respecting the electrolysis of fused lead chloride, if the writer's memory is correct, that great philosopher also remarked that the amount of chlorine evolved did not correspond theoretically with the amount of current as indicated by the voltmeter, and it seems just as likely, if the report in the Society's Journal is correct, that the extra amount of current consumed should be attributable to the electrolysis of the lead oxide in the lead oxychloride above mentioned,

as to the solution of the metallic lead in the fused lead chloride.

Indeed, this latter seems to the writer most improbable. The presence of the cloud of metallic lead in the electrolyte under the circumstances above stated, and the evolution of oxygen (not of chlorine) at the anode, while a little lead dripped from the carbon cathode, all seem to negative such a conclusion, and point to a far simpler way of accounting for the apparent anomaly than by finding in it an exception to Faraday's law.

ON NATIVE TELLURIUM FROM THE HANNAN'S DISTRICT, WESTERN AUSTRALIA.

By R. W. EMERSON MACIVOR, F.I.C., &c.

WHILE examining some specimens of telluride ore from the Hannan's district, Western Australia, I found, associated with pyrites, a finely granular, white, metallic-looking mineral, which, on analysis, proved to be tellurium. Freed from foreign substances it had a specific gravity of 6.2 and contained—

Te.. .. .	96.935
Au.. .. .	2.399
	99.334

Iron and sulphur were present, but I failed to detect any trace of selenium.

In only one other locality in Australia has native tellurium been found, viz., in the Ballarat district, Victoria.

The Chromium Syndicate, Lim.,
Quality Court, Chancery Lane, W.C.

ON CHLORINE HEPTOXIDE.

By ARTHUR MICHAEL and WALLACE T. CONN.

THE marked increase in stability shown by non-metallic oxides and acids with increment of oxygen led us to re-investigate perchloric acid, with a view of preparing its anhydride. For this purpose a pure acid is necessary, and as the product prepared according to the directions given by Roscoe (*Journ. Chem. Soc.*, xvi., 82), is somewhat impure, and can be obtained in this way only with a great loss of material, we modified the method by heating the perchlorate and sulphuric acid in a vacuum. Portions of 25 grms. of salt and 100 grms. of sulphuric acid (of about 1.839 specific gravity at 15° C.) were brought into a fractionating flask,* whose low lateral tube is connected with a second flask placed in a freezing mixture, and heated under 10–20 m.m. pressure in a paraffin bath. The reaction starts at about 90° C., and perchloric acid begins to pass over when bubbles are noticeable. The heating should be gradual to prevent frothing. In about an hour the bath may be raised to 160°, and it is kept at that temperature until all the perchlorate is dissolved, the operation usually taking about two hours. It was found impossible to decompose all the perchlorate, as the process becomes reversible towards the end, and 1.5–2 grms. of salt are easily regained from the cooled contents of the flask. The crude acid contained traces of sulphuric and hydrated perchloric acids, which were removed by a subsequent fractionation of the freshly prepared substance in a vacuum. The yield was 85–90 per cent of the theory, if allowance was made for the regained salt.

The acid was usually very slightly coloured and differed in some of its properties from the substance described by

Roscoe. Under 11 m.m. pressure its vapour heated a thermometer to 19° C. In a glass-stoppered bottle the colourless oil coloured on standing, even when kept from light, and after three weeks was quite dark, but this sample did not explode, although it was kept several months. In contact with paper or wood it exploded with a slight blue flame, carbonising but not igniting the material. In small amounts it could be mixed with well-cooled absolute alcohol without explosion, apparently with ester-formation, as was also the case when dry ether was used. To 5 grms. dry benzene, placed in a freezing-mixture, 1 grm. acid was added, and the cooled tube sealed. The acid dissolved, forming a green solution, which soon deposited a carbonaceous substance, increasing in amount until the green colour disappeared. The tube opened under slight pressure, and no free acid could be detected in the solution. Iodine dissolved in the well-cooled acid, using the proportion of 0.5 atom to 1 molecule, to form a dark solution, which, exposed to bright light, gradually changed into an almost white substance. The tube opened under slight pressure, and the gas contained a little chlorine. On heating the substance gave off iodine, leaving a white body, which, after dissolving in water, showed tests for iodic acid.*

The most interesting behaviour of perchloric acid is towards phosphorus pentoxide, and to perform this experiment successfully it is necessary to adhere strictly to the following directions:—In a small glass-stoppered retort, connected with a drying-tube filled with phosphorus pentoxide and placed in a freezing-mixture of ice and salt, 10 grms. of phosphorus pentoxide are brought, and, by means of a long tube which is bent inward and contracted at the delivering end, and has a rubber ball attached to the other end, not more than 10 drops of perchloric acid are added, waiting ten minutes before adding a second portion. It is advisable to allow the acid to drop on the sides of the retort, and the temperature of the freezing-mixture should be kept below –10° C. The retort, left in the freezing-mixture, is allowed to stand for a day, then connected with a well-cooled receiver, and slowly warmed in a water-bath to 85° C., when the new oxide passes over. The product obtained in this way is practically pure, and may be used for the experiments described below, but the freshly prepared substance may be re-distilled under ordinary pressure without danger, when it passes over at 82° C. (corr.). It should be well borne in mind that, even though the above directions for preparing the crude oxide are followed, the apparatus may be virtually pulverised by a violent explosion, and that the personal precautions necessary for work of this kind must be always observed.

Chlorine heptoxide is a colourless, very volatile oil, that on standing a day begins to turn yellow, after two or three days is greenish-yellow, with the liberation of a greenish gas. In comparison with the previously known oxides of chlorine it shows a remarkable stability, and, although when brought in contact with a flame, or by a sharp percussion, it explodes with great violence, it may be poured on paper, wood, or similar organic matter with impunity, the oxide simply volatilising in the air. Brought into a well-cooled tube with some stick sulphur and the tube corked, no reaction occurred, even after standing several days; and what is a more striking evidence of its stability, it may be poured on a cooled piece of phosphorus and remain for some days without being attacked. With cold water it sinks to the bottom of the vessel and passes slowly over into perchloric acid, but in a closed vessel it requires some days' standing before the peculiar odour of the oxide has disappeared. Dry and cooled benzene dissolves the oxide, and after a short time a reaction ensues. With iodine a reaction occurs slowly in the dark, more rapidly in the light, with liberation of chlorine and

* The neck of the flask was contracted and the air-tube fitted in tightly by means of asbestos paper, which was covered by a piece of rubber tubing; a similar joint was used between this flask and the receiver. Attached to the air-tube was a P₂O₅ drying-tube, and between the receiver and manometer a calcium soda lime tube.

* In the last number of the *Annalen* (cccx., 369), which we have just received, Vorländer and von Schilling describe a similar method of preparing the acid, although their yield is not as favourable as ours. Their acid also appears to be somewhat more explosive, which may be due to their using a perchlorate not entirely free from chlorate,

formation of a white solid. This substance begins to decompose at 380°C ., forming iodine and oxygen, and apparently represents the heptoxide of iodine. Bromine, under similar conditions, is without action.*—*American Chemical Journal*, xxiii., No. 5.

THE ALLOTROPIC FORMS OF SELENIUM.†

By A. P. SAUNDERS.

(Continued from p. 264).

Conclusions from Dilatometric Experiments.

It may seem that the experiments with the dilatometer have been needlessly multiplied. This repetition is due in part to the fact that the method of working was at first very imperfect, but mainly to the fact that the evidence to be obtained from them is both positive and negative. There is to be found in many of the text-books a description of the gray form of selenium obtained by heating the vitreous modification to 100° , which separates this as a distinct modification from the black crystals obtained in other ways, and these experiments were begun with the expectation of finding two such distinct forms with a real transition point. It will be seen, however, that the evidence is all against the existence of any stable form except the one having a density of 4.8 and the multiplicity of the experiments only serves to render that evidence more conclusive. When selenium is heated in liquids in which it is somewhat soluble, like quinoline or aniline, or in which it is practically insoluble, as paraffin, only two modifications are obtained, the vitreous and the metallic. The metallic form is a stable throughout its range, up to 220° or nearly; whereas the vitreous form goes over at any temperature above about 60° to 80° according to the liquid present. When vitreous selenium is placed in water, it behaves in the same way as it does in other liquids which do not dissolve it. Furthermore, with regard to the behaviour of the element at 200° , only one form can permanently exist there. It makes no difference whether fused selenium be cooled to 200° , or whether vitreous selenium be rapidly heated to 200° , or again, whether it be allowed to go over at any lower temperature and then raised to that point—the final density at 200° is always the same, and lies along the density curve for metallic selenium. Sunlight causes no change of volume in metallic selenium either at ordinary temperatures or at higher ones, up to 200° . It is not as a rule possible to raise the temperature of vitreous selenium above about 140° without a sudden change into the metallic form, but it may occasionally, by rapid heating, be brought to 180° or above before the change takes place. When metallic selenium is kept at ordinary temperatures or placed in a bath heated to 40° , 50° , or 60° , or any higher temperature, below 220° , it shows no tendency to go over into any other form.

The general character of the curves obtained by plotting the results of dilatometric determinations with selenium is illustrated by the accompanying drawing (Fig. 2).

The line A represents the metallic form; the line B, the fusion, with formation of liquid selenium; this when cooled gives the line C; if the cooling be stopped at 200° we obtain the line C_1 leading back to A; if it be stopped at 100° , we get the line C_2 also leading back to A. Finally, if the line C be followed down to ordinary temperatures, it is not usually possible to reproduce it with rising temperature, but the change follows a curve of the general

form of D, which again leads us back to the line A, for the metallic modification.

Two objections may be urged against conclusions drawn from dilatometric measurements regarding the possible transformation of a substance. In the first place, the results only apply to cases where the material studied is in contact with a liquid, in which it will always be more or less soluble; and in the second place, the results, being really only density determinations, will fail to bring out such changes as involve very slight alteration in specific gravity. This latter objection must be let stand, although the probability is always in favour of two different modifications having differences in density which lie within the range of experimental proof. To meet the first objection, a few density determinations were made, to fill out the gaps left in earlier investigations along this line. They will be found recorded under the corresponding heading.

Vitreous selenium is stable, by itself, at ordinary temperatures, for an indefinite time. Hittorf states that it remains for years without alteration, and the fact that the selenium of commerce is in the vitreous form further demonstrates its permanence.

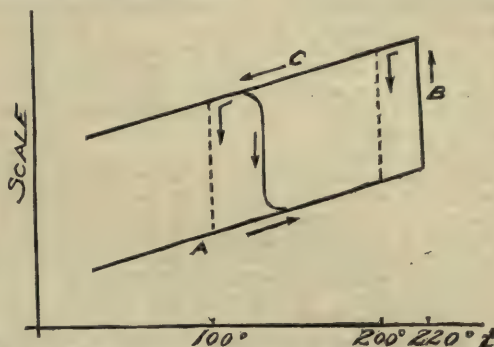


Fig. 2.—The vertical dotted lines, beginning at the right, should be lettered C_1 and C_2 . The intermediate curved line is the line D.

To illustrate the degree of its viscosity, a rod of it, having a diameter of about 5 m.m., was fastened in a horizontal position, and a weight of 200 gr. hung upon it at a distance of 6–8 c.m. from the point of support. No change could be observed in it at the end of a week. On the other hand, when the substance is fused and drawn into stout threads, and these are fastened horizontally, they bend almost at once by their own weight alone.

The vitreous and amorphous forms being both of them liquid selenium, but in different states of division, it follows that their solubilities must also be practically identical. Nevertheless, while the solubility of the amorphous form in carbon disulphide is always admitted, it will be found stated here and there that the vitreous form is nearly or quite insoluble in that liquid.

Thus Schützenberger (*Chimie Générale*, i, 438), after contrasting the solubility of the amorphous form with the insolubility of the metallic, adds:—"Vitreous selenium is also almost insoluble in carbon disulphide." But many points in the description of selenium, in this, as well as in most of the other text-books, are quite at variance with the truth, often, indeed, in disagreement with facts which have long been known. To show that vitreous selenium does dissolve in carbon disulphide, it is only necessary to place a piece in a little of this liquid for a few moments, and follow the immediate change of colour.

The data regarding the solubility in this liquid—and they apply equally for the amorphous modification—are as follows:—Mitscherlich (1855) states as a result of his experiments that one hundred parts of carbon disulphide at 46.6° dissolve 0.1 part of amorphous selenium,

* It is proposed to examine the behaviour of concentrated solutions of chloric and bromic acid towards P_2O_5 . The stability of chlorine heptoxide may be explained on lines similar to those which I (*Zeits. Prakt. Chem.*, [2], ix., 328), have given for carbon tetrachloride. This subject, which has a very important bearing on chemical affinity and on valency, will be more fully discussed in a later paper.

† From the *Journal of Physical Chemistry*, vol. iv., No. 6.

and at 0°, 0.016 part. Rammelsberg (1874) says that one part of selenium (probably amorphous) is soluble in 1376—2464—3746 parts of carbon disulphide at 20°. We have no details of either of these determinations, but Mitscherlich had noted for the vitreous form as well as the amorphous, that on standing in contact with carbon disulphide, red crystals appear, and he had interpreted this in the case of the vitreous form as not being a change in the mass of the material, but a superficial alteration involving successive solution and re-crystallisation.

To determine the correctness of this explanation I placed some pieces of vitreous selenium in carbon disulphide, and left them in diffused daylight. On the following day the surfaces were found to have lost their black vitreous lustre, and to have acquired a dull brownish iridescence; they were, moreover, everywhere covered with minute, but well-formed, glittering, transparent red crystals, some of which were loose in the bottom of the vessel, but most of them adhering to the mass of the selenium. After twelve days more, there was no further visible change. The fragments were then removed from the solution, and when broken were found to have their original black fracture within. This shows that Mitscherlich's explanation is correct. The change does not extend within, but stops as soon as the entire surface has become coated with crystals or a crystalline film. It shows also that in all likelihood the crystals are much less soluble than the original material; otherwise this change would be difficult to explain. My experiments have further shown that the change goes on much more rapidly than Mitscherlich supposed.

Now the observation just recorded goes far to clear up the discordant solubility results of Rammelsberg. It is probable that they were obtained by successive determinations from the same material, and that their variation corresponds to the change going on in the solution as it passed from a state of saturation with respect to amorphous selenium, to a state of saturation with respect to the red crystals themselves. Hence, while his first value according, as it does, fairly well with Mitscherlich's, probably represents the solubility of amorphous selenium, the second represents nothing definite at all, and the third is possibly somewhere near the value for the red crystals.

A further experiment of mine showed that vitreous selenium in carbon disulphide in the dark, remained unchanged for six days. At the end of that time, it was allowed to stand in the light for a day, and was then found covered with crystals.

Vitreous and amorphous selenium are known to be soluble in various other liquids, but few quantitative measurements have been made.

Reigers (1893), using the powder of commercial vitreous selenium, found its solubility in methylene iodide at 12°, to be 1.3 parts in 100; from this solution, on evaporation, the selenium separates in monoclinic, blood-red leaflets, and also in black opaque aggregations, the latter probably metallic selenium. Schneider (1866) found that when amorphous selenium is allowed to stand in contact with selenious bromide for eight days, with occasional heating to 70°—80°, a solution is obtained which contains in 2 gr. of the solvent—probably at ordinary temperatures—0.44 gr. selenium.

Rathke (1869), in endeavouring to find a liquid which would yield good crystals of the metallic form, noted the solubility of vitreous selenium in carbon di-selenide, selenium di-ethyl, sulphur di-ethyl, and in selenious chloride, which last is capable of taking up very considerable quantities of the element. All forms of selenium dissolve in sulphuric acid, forming a green solution, but no exact study has been made of the degree of solubility. Some further notes on solubility will be found later on, in the description of the other modifications.

Petersen (1891) found it impossible to get vitreous selenium quite pure. He found that samples prepared by rapid cooling of the fused mass were never free from material which was insoluble in carbon disulphide, though

his difficulty may possibly have arisen from impurities in the material.

Regnault, in studying the rate of cooling of melted selenium to find whether there were any irregularities in the change of temperature, made a series of observations between 260° and 40°, and found no signs of any irregularity. The apparatus consisted merely of a vessel filled with a large quantity of selenium, with a thermometer standing in the mass. In order to confirm this result, he placed the apparatus in an air-bath at 100°. The readings, which were taken every minute, are as follows:—

241°6	175°95	148°1°	137°85°
229°8	170°9	146°3	137°0
219°3	166°4	144°7	136°25
210°2	162°4	143°25	135°5
201°7	158°8	142°0	134°7
194°4	155°6	140°75	133°9
187°6	152°9	139°65	133°2
181°6	150°4	138°75	

From here on, the readings were made every five minutes—

133°2°	115°0°	114°05°	116°0°
129°2	113°4	115°9	113°35
125°35	112°8	117°9	111°25
121°9	112°6	120°75	109°65
119°1	112°55	121°3	108°75
116°8	113°0	118°9	107°55
			106°8

It will be seen that at about 113° there is a marked rise of temperature, followed by a uniform drop like that which preceded. What the cause of this may have been, it is impossible to say; perhaps a partial transformation into metallic selenium, although at that temperature the transformation should have been complete if it had taken place at all; possibly a transformation into one of the red crystalline forms; or possibly merely an experimental variation. At any rate, the observation being of an exceptional character, is worth recording.

Electrification of the Vitreous Form.

Seebeck (1826) reports that a rod of selenium (no doubt the vitreous form) becomes negatively electrified when rubbed, though less strongly than sulphur.

Reiss (1845) confirmed this observation of Seebeck. Berzelius had been unable to observe this phenomenon, though he records in his "Lehrbuch" that it was noted by Bondsdorff.

My experiments showed that vitreous selenium, when freshly prepared by pouring the melted material on a cold stone slab, shows very marked electrification.

Refraction and Dispersion of Vitreous Selenium.

These properties were investigated by Sirks (1871) who found the following values—

n_A	n_a	n_B	n_c	n_c	n_D
2.653	2.691	2.730	2.786	2.857	2.98

Thus the element shows strong dispersive power, as well as very high refraction.

Diathermancy.

Schultz-Sellack (1869) furnishes the following data for the diathermancy of vitreous selenium—

Thickness of the selenium plate. M.m.	Percentage of heat passed through—	
	From lamp-black at 100°.	From an illuminating gas flame.
0.4	50	36
3.0	16	5

(To be continued).

ON THE FILTERING VALUE OF OLD ALLUVIAL DEPOSITS.

By Dr. F. MALMÉJAC.

WITH a view to estimating the filtering value of old and new alluvial deposits, we have examined the water borne by these different formations, and here give our first results.

The water examined came from the underground reservoir in the old gravels of Meurthe-et-Moselle. It was pumped up from a well sunk in the midst of highly cultivated land, which was manured every year. This well was 5 metres in depth, and the water level was 2 metres from the bottom. The samples were taken from a point intermediate between the surface of the water and the bottom. At the moment of taking each sample, the pump had been at work for twelve hours.

The first samples were taken before the application of manure, after a prolonged period of rain, snow, and thaw.

The last were taken four months after manuring with farmyard manure, during which months there had been on several occasions several days of rain followed by a long drought.

At the time of taking both samples, the pump was first made to deliver a large quantity of water, which then ran perfectly clear and limpid. The analyses of these samples for the two periods have given the following results:—

	Before manuring.	After manuring.
Hardness . { Total	14°	15°5'
{ Permanent	2°	1°
Residue at 100°	280	330
Colour of residue	Reddish	Grey
Sulphates, as H ₂ SO ₄	0	Distinct traces
Chlorides, as NaCl	0	Do.
Nitrates, as HNO ₃	10	Traces
Nitrites	0	0
Lime	110	145
Magnesia	0	Traces
Silica	11	Do.
Peroxide of iron	Traces	2
Organic matter in { Alkaline	1	5°0
{ m.grms. of oxygen		
{ per litre { Acid ..	1	5°2
Oxygen	10	7°4
Free ammonia	0	0°32
Albumenoid ammonia	Traces	0°40

The above results are expressed in m.grms. per litre.

These analyses show that, before the manuring, the water examined was quite fit for drinking purposes; after manuring, it had to be condemned.

A single analysis, however, is not sufficient on which to form an opinion of the fitness of a water for human use; before deciding definitely, it is necessary to examine several samples taken at different times.

The old alluvial deposits of Meurthe-et-Moselle, and probably all other alluvials of the same date, are, however, very bad filters, even in a thickness of 5 metres; not only do they allow organic matter to pass, but also all kinds of bacteria, as was conclusively shown by Dr. Imbeaux in his thesis on the potable waters of Meurthe-et-Moselle (Nancy, 1897).

In the case now under consideration, it is undeniable that the gravels have allowed the organic matter from the manure spread over the surface to reach the underground water.

This contamination is manifest by the considerable increase in the organic matter—the animal nature of which cannot be denied when we take into account the increase in the lime, sulphates, and chlorides, and, above all, the free and albumenoid ammonia which accompany it—while at the same time we see a diminution in the oxygen and in the nitrification,

Experiments now going on, and which will be published in due course, enable us to foresee that modern alluvial deposits, of the same thickness of 5 metres, are still worse filters than the older gravels.

It is therefore necessary whenever we have to pronounce an opinion on the value of a water for drinking purposes, to be extremely careful, when the supply is from alluvial gravels, if we have not had an opportunity of properly studying the surroundings of the source of supply.

We are, however, of the opinion that, whenever possible, it would be as well not to use water direct from alluvial gravels, as we have just shown that, with a thickness of 5 metres, this material is of no value whatever as a filter.

—*Journ. de Pharm. et de Chim.*, Series 6, vol. xii., No. 8.

ANALYSIS OF THE WATERS FROM THE HOT SPRINGS AT DJEBEL ACHKEL.

By M. PUAUX.

AT the foot of the Djebel Achkel, on the border of Lake Achkel, connected with the Lake of Bizerta by means of the Tindja, are three baths supplied by hot springs. During that period of the year when the region is accessible, these baths are much frequented by the Arabs.

The installation of these baths is of rudimentary simplicity. A natural basin, of about 4 metres area and 1·4 metres in depth, is covered over by the interlaced branches of the surrounding trees; the water rises naturally from the bottom of each basin and runs away over the edges. This bower is entered by an opening 1·5 metres in height.

The Arabs use these waters for the treatment of rheumatic affections, for which purpose they make superficial incisions in their limbs and then plunge them several times a day into the water. They also use these baths for the treatment of skin diseases, fevers, and probably all the ills their flesh is heir to.

These three baths are named as follows:—

Hammam *Sidi-bel-Abbés*, with a temperature of 45°; Hammam *Ain-Khalifif*, with a temperature of 43°5'; and Hammam *El-Djerab*, with a temperature of 43°.

The waters are all three limpid, and only have a little organic detritus floating on their surface, due to insufficient protection.

Chemical analysis shows that the composition of these three springs is identical, and that they come from a common subterranean source.

Composition of these Waters.

Density at 20°	1010
Residue dried at 120°	13°210
Residue heated to red heat ..	12°885
Sulphuric acid	1°907
Chlorine	5°515
Carbonic acid	0°098
Lime	1°707
Magnesia	0°780
Soda	2°973
Potash	0°270

The total weight of the different elements estimated is 12°85 grms., which agrees very closely with the residue heated to red heat.

The probable grouping of these elements is—

Sulphate of potash	0°499
Sulphate of magnesia	1°140
Sulphate of lime	1°560
Carbonate of lime	1°221
Chloride of lime	1°866
Chloride of sodium	7°563

A fourth spring actually rises under the waters of the

lake. We propose making an examination of this water in the course of a month or two.

These analyses lead us to the conclusion that the waters contain principally sodic chloride, and have a great analogy with those of the *Hamman-Lif* and *Bourbonne-les-Bains*.—*Journ. de Pharm. et de Chim.*, Series 6, vol. xii., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 15th, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

MESSRS. F. C. Britten, G. C. Thomson, R. G. Halstead, and J. A. Mathews were formally admitted Fellows of the Society.

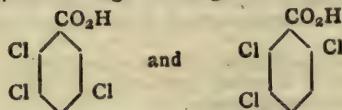
The following certificates were read for the first time:—Messrs. H. H. Cousins, Government Laboratories, Kingston, Jamaica; Robert Dodd, 28, Sibella Road, Clapham, S.W.; Arthur Houldershaw, 71, Lavender Gardens, West Jesmond, Newcastle-on-Tyne; Edward Hughes, Rectory, Barmouth; Robert Salmon Hutton, Owens College, Manchester; Stephen Archigenes Ionides, Balliol College, Oxford; Robert Henry Jones, Glen Albyn, Coity Road, Bridgend, Glam.; H. T. G. van der Linde, 101, Tyndall Avenue, Toronto, Canada; William Meredith, 63, Albion Place, Ulverston; James Moir, The Ash, 62, Hamilton Place, Aberdeen, Scotland; H. M. Smith, 79, Helix Road, Brixton, S.W.

Of the following papers, those marked * were read:—

*147. "Trichlorobenzoic Acid." By FRANCIS EDWARD MATTHEWS.

The hexachloride of benzonitrile is acted upon by alcoholic sodium hydroxide, forming a mixture of trichlorobenzoic acids, which, on fractional crystallisation of the barium salts, was found to give a new trichlorobenzoic acid.

At present four of the six possible trichlorobenzoic acids are known, the missing two being—



As the new acid was found to yield an ester readily when treated with hydrogen chloride and alcohol, which an acid having the second of the above formulæ should not do, both positions adjacent to the carboxyl group being occupied by chlorine, the former of the two formulæ may be taken as proved.

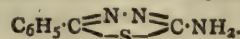
By the action of quinoline upon the nitrile, $\text{C}_6\text{H}_5\text{Cl}_3\text{CN}$, followed by steam distillation, the nitrile of the new acid, $\text{C}_6\text{H}_2\text{Cl}_3\text{CN}$, is easily prepared in a state of purity. It crystallises from aqueous alcohol in long, white, lustrous needles melting at 87° . After hydrolysis with alcoholic sodium hydroxide, the acid, which crystallises from water in small needles melting at 163° , is readily obtained.

The following salts have been prepared:— $(\text{C}_6\text{H}_2\text{Cl}_3\text{CO}_2)_2\text{Ba} + 3\text{H}_2\text{O}$; $(\text{C}_6\text{H}_2\text{Cl}_3\text{CO}_2)_2\text{Sr} + 3\text{H}_2\text{O}$; $(\text{C}_6\text{H}_2\text{Cl}_3\text{CO}_2)_2\text{Ca} + 4\text{H}_2\text{O}$; $\text{C}_6\text{H}_2\text{Cl}_3\text{CO}_2\text{Ag}$. The acid chloride, $\text{C}_6\text{H}_2\text{Cl}_3\text{COCl}$, melts at 36° ; the amide, $\text{C}_6\text{H}_2\text{Cl}_3\text{CONH}_2$, crystallises in small needles which melt at $204\text{--}205^\circ$.

The ethyl ester, $\text{C}_6\text{H}_2\text{Cl}_3\text{CO}_2\text{Et}$, is obtained by the action of hydrogen chloride and alcohol upon the acid. It is a liquid volatile with steam, and possessing, but in a lesser degree, the odour of ethyl benzoate.

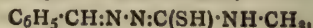
*148. "Oxidation of Benzalthiosemicarbazone." By GEORGE YOUNG, Ph.D., and WILLIAM EYRE, B.Sc.

Benzalthiosemicarbazone, $\text{C}_6\text{H}_5\text{CH:N:N:C(SH)NH}_2$, is oxidised by ferric chloride to amidophenylthiodiazole,—

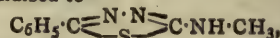


The base melts at $222\text{--}223^\circ$, its hydrochloride at $213\text{--}214^\circ$. The methyl derivative, $\text{C}_6\text{H}_5\text{C}_2\text{N}_2\text{SCH}_3\text{NH}_2$, is an oil; its platinichloride, $[\text{C}_6\text{H}_5\text{N}_3\text{S}]_2\text{H}_2\text{PtCl}_6$, melts at 218° . The acetyl derivative, $\text{C}_6\text{H}_5\text{C}_2\text{N}_2\text{SNHCOCH}_3$, which melts at 276° , is an acid forming stable sodium and silver salts. Both the methyl and acetyl derivatives yield the same methylacetyl derivative, $\text{C}_6\text{H}_5\text{C}_2\text{N}_2\text{SCH}_3\text{NCOCH}_3$, which melts at 144° .

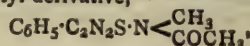
Benzal-4-methylthiosemicarbazone,—



is similarly oxidised to—

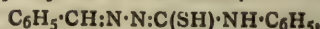


methylamidophenylthiodiazole, which melts at $183\text{--}184^\circ$. Its platinichloride, $[\text{C}_6\text{H}_5\text{N}_3\text{S}]_2\text{H}_2\text{PtCl}_6$, melts at $208\text{--}209^\circ$. The acetyl derivative,—

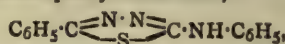


melts at 195° .

Benzal-4-phenylthiosemicarbazone,—



yields phenylamidophenylthiodiazole,—



previously described by Marckwald. Its silver derivative, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{SAg}$, decomposes with explosive violence when suddenly heated.

*149. "The Nitration of Benzeneazosalicylic Acid." By J. T. HEWITT and J. J. FOX.

One of the authors has already pointed out (Hewitt, *Trans.*, 1900, lxxvii., 99) that when dilute nitric acid is warmed with benzeneazophenol a substance results in which the nitro-group has entered the phenol nucleus in the ortho-position relatively to the hydroxyl. No melting, on the other hand, by nitrating benzeneazophenol in strong sulphuric acid, obtained paranitrobenzeneazophenol (*Ber.*, 1887, xx., 2997).

The authors have studied the action of nitric acid on benzeneazosalicylic acid under varying conditions, and find that with dilute acid at $65\text{--}70^\circ$ the nitro-group enters the salicylic residue in the ortho-position relatively to the hydroxyl. The constitution of the resulting compound was determined by comparison with the product obtained from phenyldiazonium chloride and nitrosalicylic acid ($\text{CO}_2\text{H} : \text{OH} : \text{NO}_2 = 1 : 2 : 3$).

Benzeneazoorthonitrosalicylic acid melts at 197° (uncorr.), its methyl ester at $132\text{--}134^\circ$, and the ethyl ester at $128\text{--}129^\circ$.

By the nitration of benzeneazosalicylic acid dissolved in concentrated sulphuric acid, paranitrobenzeneazosalicylic acid, identical with the substance described by Meldola (*Trans.*, 1885, xlvii., 666), was obtained. Its ethyl ester melts at $220\text{--}225^\circ$.

*150. "Upon the Collection and Examination of the Gases produced by Bacteria from certain Media." By WALTER C. C. PAKES and WALTER H. JOLLYMAN.

The authors described a new apparatus for the collection of the gases produced by bacteria when grown either under aerobic or anaerobic conditions.

Experimenting with the *Bacillus pyocyaneus*, which is supposed to be a strictly aerobic organism, they found that it grew in media containing 1 per cent of potassium or ammonium nitrate under the strictest anaerobic conditions as the term is at present understood (that is, in the presence of hydrogen, or in the absence of any gas). They concluded, therefore, that the terms aerobic and anaerobic must be extended to include the presence of oxygen in the form of nitrates.

Upon analysing the gases produced by this organism from media containing nitrates, they found that both free oxygen and free nitrogen were evolved, the former in small quantities, but constantly.

151. "The Bases contained in Scottish Shale Oil." By FREDERIC CHARLES GARRETT, M.Sc., and JOHN ARMSTRONG SMYTHE, B.Sc., Ph.D.

Though many investigators have examined the bases contained in coal-tar, but little attention has been paid to those present in shale oil; the authors have therefore undertaken the examination of those obtained from the Broxburn oil. The shale, on distillation, yields gas, ammonia water, and "crude oil"; this "crude oil" is again distilled, giving "green naphtha," "green oil," and "still coke," the temperature towards the end of the operation rising to a red heat. A quantity of this "green naphtha" was washed with a $\frac{1}{2}$ per cent of sulphuric acid (diluted to about 15 per cent). Steam was blown through the reddish-brown liquid so obtained for several hours, to free it from a small quantity (about 0.1 per cent) of an oily liquid possessing a peculiarly disgusting smell; when this had been removed, sodium hydroxide solution (17½ per cent) was added, and superheated steam blown through until all the volatile bases had been driven over. The soluble bases in the distillate were thrown out by the addition of solid sodium hydroxide, the mixed bases were then dried by solid potash and fractionally distilled; each litre of the crude acid liquor yields about 120 grms. of the dry bases, of which about 25 per cent boil below 170°, and 46 per cent between 170° and 205°.

The basic oil thus obtained was then repeatedly refractionated, and an attempt made to isolate the various bases in the lower fractions by precipitation with mercuric chloride and fractional crystallisation of the salts so obtained. The portion boiling below 125° (about 10 grms.) was examined for pyridine by precipitation with potassium ferrocyanide, but none was found, the base being chiefly α -picoline (b.p. 128°); from the other fractions below 160° the symmetrical collidine ($\gamma\gamma'$ -trimethyl pyridine) and two other bases which appear to be the hitherto undescribed lutidines ($\alpha\beta$ - and $\alpha\beta'$ -dimethyl pyridine). The first of these boils at about 160° and yields a platinumchloride melting with decomposition at 208°, whilst the second boils at about 140°, and although no platinum compound was isolated it yielded a gold compound melting at 73°; in each case, however, the amount of base obtained was very small. Having now obtained between 2 and 3 kilogrammes of the raw bases, the authors are attempting a more systematic examination of them.

The authors have to thank Mr. George Beilby for calling their attention to the necessity for this work, and Mr. D. R. Stuart for kindly providing them with the raw material they required.

152. "On a Simplified Method for the Spectrographic Analysis of Minerals." By WALTER NOEL HARTLEY, F.R.S., and HUGH RAMAGE, A.R.C.Sc.I.

The authors pointed out that some of the rare earths are very difficult to detect, and others more widely diffused are not easily separated and recognised either by the ordinary methods of chemical analysis or by spectroscopic examination. A simplification of the method of obtaining oxyhydrogen blowpipe spectra (Hartley, *Phil. Trans.*, 1894, clxxxv., 168) was described and examples given of its application to the analysis of various metallurgical products, metallic ores, and siliceous minerals. The method is to burn the metals, minerals, or precipitates, on ashless filter-papers in an oxyhydrogen flame, and to photograph the spectra in the usual way. Refractory silicates in very fine powder are decomposed by being heated with strong sulphuric acid and ammonium fluoride which has been purified by distillation in a platinum retort. After the complete decomposition of the mineral, the sparingly soluble sulphates are separated by filtration and burnt on the ashless paper. The hydroxides of the heavy metals are precipitated by ammonia and similarly burnt.

The alkalis are contained in the aqueous solution of which the treatment is varied according to the nature of the substance under examination. For the separation of rubidium and cesium, platinic chloride is used and the platinumchlorides collected and burnt.

Rammelsberg Memorial Lecture.

The Rammelsberg Memorial Lecture will be delivered by Professor H. A. Miers, D.Sc., F.R.S., on Thursday, December 13th, 1900, at 8.30 p.m.

NOTICES OF BOOKS.

Thirty-sixth Annual Report on Alkali, &c., Works. By THE CHIEF INSPECTOR. London: Eyre and Spottiswoode. 1900. Pp. 184.

THIS Report is on the Proceedings under the Alkali, &c., Works Regulation Acts during the year 1899.

The number of Works now registered under the Acts in England, Ireland, and Wales, is 1055. Of these 88 only are works decomposing salt, while the remainder carry on processes which are scheduled under the Acts of 1881 and 1892.

These numbers show a net increase of two alkali and one other works since the previous year. There are also 127 works registered in Scotland, bringing the total number up to 1182.

With regard to the escape of acid gases, two changes have been made; the first is to bring the statistics presented more into conformity with the wording of the Act of 1881, viz., the amount of hydrochloric acid condensed in place of that escaping by the chimney, is presented. Section 3 (a) of this Act provides for the condensation "of the muriatic acid evolved in such work, to the extent of 95 per cent," &c. The figures for 1897, 1898, and 1899 show 98.39, 98.53, and 98.60 per cent condensation respectively. The second change is an addition of the average escape of hydrochloric acid in salt-works. In 1884 the escape of hydrochloric acid in the extraction of salt from brine was put under the same limits of escape by the chimney as in alkali works, viz., 0.20 grain per cubic foot of chimney gases; it is therefore considered right to present this average figure annually in the table.

There have been 5011 visits and 5585 tests made during the year, and four prosecutions; though this latter figure is higher than usual, it can by no means be considered excessive, and we are glad to see that in the larger works there has been this year very little cause for anxiety, and much cause for praise in the efficiency of plant, and in the control attained over local escapes, as well as over those where the limits are prescribed by the Act.

The activity which has been so noticeable in the Leblanc process during the year 1899 has, of course, extended to the production of bleaching-powder and chlorates, and there has also been an increase in the production of chlorine by electrolytic processes.

The most striking event of the year 1899, in connection with the Leblanc industry, was the terrible explosion of 156 tons of chlorate of potash at the Kurtz works of the United Alkali Company, on May 12. By this explosion five men lost their lives, and a number of persons were injured. A special inquiry was held by Colonel Ford, C.B., into the circumstances attending the explosion, and his report has been issued as a Parliamentary paper. A curious and interesting effect of this explosion was noticed on the barometer at the Hardshaw Brook Chemical Works, about a quarter of a mile away; the mercury "suddenly rose, and immediately fell to a point indicated by some scum on the surface of the mercury being left behind in the barometer tube on the mercury rising again to its normal height. This point was at 22.60 inches from the surface of the mercury in the cup (corrected

indicating the vacuum created in the atmosphere after the explosion. The first effect of the explosion was a pressure which drove the mercury up above the normal height 2½ inches, until it was arrested by the closed end of the tube; . . . it then fell to 22·60 inches, and left the mark on the barometer tube mentioned. All the windows at Hardshaw Brook Chemical Works were blown inwards, but at a greater distance from the scene of the explosion the windows were blown outwards."

The Elements of Inorganic Chemistry, for Use in Schools and Colleges. By W. A. SHENSTONE, F.R.S. London: Edward Arnold. 1900. Pp. 506.

THE author's endeavour, in compiling this volume, was to provide a book which begins with experimental work for quite young students, and develops in the later stages into a text-book suitable for the older ones. The subject matter has been divided into numbered sections, which is not only useful for purposes of reference, but also enables the teacher to modify the course to the abilities of his various pupils and the time at their disposal.

The sections on carbon include a good deal that is usually omitted from books on inorganic chemistry, and there is a large number of references; these, if properly used, will of course be of considerable advantage, but most students have not the run of a good library, even if they have the inclination to use it.

The general arrangement of the book is good, and should help the teacher to lay a solid foundation in the minds of his pupils, ready for the additional load of more advanced work.

A Systematic Handbook of Volumetric Analysis; or the Quantitative Estimation of Chemical Substances by Measure, applied to Liquids, Solids, and Gases. By FRANCIS SUTTON, F.I.C., F.C.S. Eighth Edition, Enlarged and Improved. London: J. and A. Churchill. 1900. Pp. 640.

As speed is a very important factor in technical chemical estimations, it naturally follows that the use of volumetric methods should become more and more developed; many new processes have been made known since the publication of the last edition of this book, and this fact has caused some delay in the issue of the present edition, owing to the time it takes to find whether there is any real value in the new methods or in the modifications of the old ones; an endeavour has, however, been made to insert only those which have been actually tested and found to be of real use.

The general plan of the book is the same as in previous editions, but there are of course many important additions; for instance, as an Appendix to Part V. the author gives two new methods for the estimation of potash. The first was devised quite recently, during the printing of this book, and too late for notice in its proper place. This method is based on the fact that potash may be combined in an insoluble form as cobalti-nitrite of sodium and potassium, $K_2NaCo(HO_2)6H_2O$, and the amount of potash is found by using standard potassium permanganate as an oxidising agent, 1 c.c. of strictly N/10 permanganate being equal to 0·0007833 grm. of K_2O ; the author's experience is that with careful management very fair results may be obtained. The second method referred to is based on the formation of the double thiosulphate of bismuth and potassium and its estimation by iodine. Among the drawbacks to the method are the highly concentrated solution of the potash required and the large amount of pure alcohol necessary to be used. The end-point is somewhat difficult to distinguish, and care is necessary to procure pure, fresh, calcium thiosulphate.

These are but an example of many other new processes and methods which have been added to the book in order that it may keep its well-known place as the standard work on volumetric analysis, a place it took nearly forty

years ago, when Mr. Sutton brought out the first edition in 1863. Since that time many striking improvements have been made in chemical technology, but as the years have rolled on new editions have kept pace with discovery, while the reputation of *trustworthiness* has always been maintained.

A School Chemistry. By JOHN WADDELL, B.A. (Dal. Coll.), B.Sc. (Lond.), &c. New York: The Macmillan Co. London: Macmillan and Co. 1900. Pp. 278.

ALTHOUGH differing widely in style from the ordinary chemistry-book for beginners, we are of opinion that this volume will be favourably received. The subject is treated in a more popular manner than young students are accustomed to meet with, and it naturally follows that, when their interest is aroused, the lectures and laboratory work are more likely to be of lasting good. Water is first discussed, as being one of the most common substances, though, according to some modern writers, even the best water is only "diluted sewage"; then follows the consideration of hydrogen and oxygen, the latter leading to the study of air and its constituents. No mention of the atomic theory is introduced until the study of a large number of facts has afforded an intelligible basis for it, until, indeed, the pupil has in his possession most of the facts upon which Dalton founded the theory; he is thus enabled to obtain an accurate view of the real meaning of formulæ, and power to use them correctly. In other words, in this volume theory is subordinated to facts.

There is one point to which already we have drawn frequent attention in other books of this class, and that is the inappropriate nature of many of the illustrations; for instance, on page 173, we read "Experiment 79.—Place a piece of filter-paper upon a tripod as in the figure (Fig. 52)," and by the side there is a figure of a tripod with a piece of paper on it; what can be more unnecessary? Then, going to another extreme, in Chapter XIX., on the "Iron Group of Metals," we find illustrations of the sections of a blast-furnace and a reverberatory furnace, as well as a Nasmyth hammer and a Bessemer converter; greater discrimination should be exercised in this matter.

We note, on p. xiii., the names of several American firms recommended for supplying the apparatus needed for carrying out the experiments described in this book. Considering the book is published in London as well as in New York, we think some English firms might also have been mentioned.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

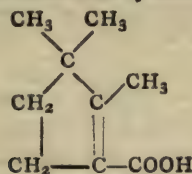
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 20, November 12, 1900.

Chemical Reactions provoked by the Silent Electric Discharge.—M. Berthelot.—The author studies the subject of silent electric discharge with regard to its chemical effect under three different sets of conditions:—1. When such a current as is developed in a gaseous layer between two surfaces of dielectric bodies is used, influenced either by the variations of potential which determine the discharge of an induction coil or an electric machine, or by the constant potential difference between the two poles of an open electric pile. 2. When atmospheric electricity is considered, such as that existing under normal conditions, apart from storms and their explosive phenomena; that is to say, the differences in potential which exist between the different layers of air or between a layer of air and

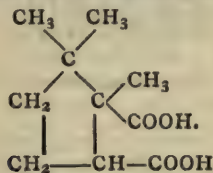
bodies situated on the earth's surface. 3. When electricity developed by inequalities of temperature is used, and that produced by chemical reactions giving rise to potential differences in the different regions of a gaseous system, constituted either of a single gas or of a mixture; or, further, between this gaseous system and liquid or solid bodies in contact with it.

Decomposition by Alkalis of Acetylenic Acetones.—Ch. Moureu and R. Delange.—A preliminary conclusion can be drawn from the experiments described in the present paper and in the authors' former paper, that, generally, boiling solutions of alkalis decompose acetylenic acetones. As to the method of decomposition, it may be remarked that benzoylphenylacetylene, acetylcyanthylidene, and benzoylcyanthylidene are decomposed into acid and ketonic products (a single acid and a single acetone in the case of benzoylphenylacetylene, on account of the symmetry of the corresponding β -diketone), while the decomposition of acetylenic acetones into acids and acetones appears to be the general rule, so that the decomposition of acetylphenylacetylene into phenylacetylene and acetic acid is an exception. The authors intend to prepare and investigate other acetylenic acetones, so as to determine, if possible, in what cases the decomposition into acetylenic and acid carbide takes place, which decomposition, up to the present, appears to be peculiar to acetylphenylacetylene.

Constitution of Camphoric Acid, and the Migrations which take place in the Molecule.—G. Blanc.—All preceding papers published by the author on the constitution of camphoric acid had for their aim the representation of isolaunonic acid by the formula—



As this acid is derived from camphoric acid by extraction of the elements of water and carbonic oxide, the formula of camphoric acid can easily be deduced, and is found to be—



Several objections have been raised to this formula. The author discusses and explains these objections.

Evolution of Terpenic Compounds in Geranium.—Eug. Charabot.—The author's experiments on geranium prove that the etherification effected is in proportion to the development of the plant. The transformation from geraniol into rhodinol is represented by the equation $\text{C}_{10}\text{H}_{18}\text{O} + 2\text{H} = \text{C}_{10}\text{H}_{20}\text{O}$, and takes place in the green parts of the plant, which, as is well known, constitute the chief reducing media. This hypothesis agrees with the chemical experiments which the author has made, and with the physiological facts already accepted.

Presence of Invertine or Sucrose in Grapes.—V. Martinand.—In the juice of all the species of grape which the author was able to procure, a decided quantity of invertine was found, which is able, under the conditions of his experiments, to invert a quantity of saccharose—almost double the quantity of original wort used. At 30°, the temperature of fermentation of grape wort, the increase of invert sugar is also considerably raised. However, the sucrose disappears completely in wines after being submitted to strong oxidation.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—Sir Robert Ball, Six Lectures (adapted to young people) on "Great Chapters from the Book of Nature."

Professor J. A. Ewing, Six Lectures on "Practical Mechanics (experimentally treated), First Principles and Modern Illustrations."

Dr. Allen Macfadyen, Fullerian Professor of Physiology, R.I., Four Lectures on "The Cell as the Unit of Life."

Dr. Arthur Willey, Three Lectures on "The Origin of Vertebrate Animals."

The Rev. H. G. Graham, Three Lectures on "Society in France before the Revolution."

Professor Percy Gardner, Three Lectures.

Sir Wyke Bayliss, Two Lectures on "Shakespeare in Relation to his Contemporaries in Art."

Professor R. K. Douglas, Two Lectures on "Government and People of China."

Mr. F. Corder, Three Lectures on "Vocal Music, its Growth and Decay" (with Musical Illustrations).

The Right Hon. Lord Rayleigh, Six Lectures on "Sound and Vibrations."

The Friday Evening Meetings will begin on January 18th, when a Discourse will be delivered by Professor Dewar on "Gases at the Beginning and End of the Century." Succeeding Discourses will probably be given by Dr. A. W. Ward (the Master of Peterhouse), the Right Rev. Monsignor Gerald Molloy, Professor G. H. Bryan, Professor J. J. Thomson, Sir W. Roberts-Austen, Mr. H. Hardinge Cunynghame, Mr. W. A. Shenstone, Dr. Horace Brown, The Right Hon. Lord Rayleigh, and other gentlemen.

On Tungsten. Preparation of Tungsten with the Help of Liquid Air.—A. Stavenhagen.—To obtain the highest possible temperature we proceed in the manner already described (*Berichte*, xxii., p. 1413; *CHEM. NEWS*, lxxxii., p. 227), but also add to the mixture in the crucible one-third of its volume of liquid air; the mass is well stirred and put on the fire; it is as well not to work on more than 50 grms. of material. The temperature soon rises nearly to a white heat, and a well-melted ingot of tungsten is obtained nearly free from aluminium. The electrolysis of paratungstate of lithium, conducted in a porcelain crucible at 1000°, with a current of 3 ampères at 15 volts, after washing the mass with water, hydrochloric acid, and a boiling solution of lithia, gives crystals of tungsten containing about 6 per cent of aluminium. But with a current of 3.5 ampères and 12 volts we obtain a tungsten-lithium bronze in fairly large bluish-black crystals; this has already been prepared by H. Scheibler. —*Berichte*, xxii., p. 3064.

Preparation of Molybdenum and Uranium with the Help of Liquid Air.—A. Stavenhagen.—We proceed as in the case of tungsten (see preceding paragraph). With molybdenum the return is low, on account of the volatility of MoO_3 . With uranium we notice that the mixture $\text{UO}_3 + 2\text{Al}$, with a slight excess of Al, burns with difficulty by itself, and the uranium does not unite in an ingot. On the addition of liquid air (20 grms. for 30 grms. of the mixture), the deflagration is very violent, accompanied by a brilliant light, and an ingot of uranium is then obtained. —*Berichte*, xxii., p. 3065.

The Compounds of Basic with Acid Colouring Materials.—A. Seyewetz.—The compounds of basic with acid colouring materials are remarkable for their insolubility in water, which appears to be the greater as the colours used have a more marked acid or basic character. This property can thus be used, in certain cases, as a delicate qualitative reaction, as in very dilute solutions a precipitate will be formed by the addition of another suitable colouring-matter. —*Bull. de la Soc. Chim. de Paris*, Series 3, xxiii., No. 12.

MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Society of Arts, 8. (Cantor Lectures). "Electric Oscillations and Electric Waves," by Prof. John A. Fleming, M.A., D.Sc., F.R.S.
- WEDNESDAY, 12th.—Society of Arts, 8. "The Treatment of London Sewage," by Prof. Frank Clowes, D.Sc.
- THURSDAY, 13th.—Chemical, 8.30. "Rammelsberg Memorial Lecture," by Prof. H. A. Miers, D.Sc., F.R.S.
- FRIDAY, 14th.—Physical, 5. (This meeting will be held in the Physical Laboratory of the Royal College of Science, South Kensington). "Electric Inertia" and "The Effect of Inertia on Electric Currents in a Rotating Sphere," by Prof. A. Schuster, F.R.S. "Exhibition and Description of a Quartz thread Gravity Balance," by Prof. R. Threlfall, F.R.S. "On the Theory of Magnetic Disturbances by Earth Currents" and "The New Physical Laboratories of the Royal College of Science," by Prof. A. W. Rücker, F.R.S. "Notes on the Practical Application of the Theory of Magnetic Disturbances by Earth Currents," by Dr. R. T. Glazebrook, F.R.S. Exhibition of a Set of Half-seconds Pendulums, by W. Watson.

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- Spon's Encyclopædia of the Industrial Arts. 2 vols., 1832, 50s.
- Pelouse et Fremy's Traite de Chimie Générale. 7 vols. 25s.
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THE CHEMICAL NEWS.

VOL. LXXXII., No. 2142.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART VI.

By HARRY BREARLEY.

(Continued from p. 260).

SULPHUR.

The following arrangement of the means of estimating sulphur is far from perfect, but, on the whole, it groups similar processes into the same section better than some other arrangements which have been suggested. In each section the items are arranged, as far as possible, with respect to the estimation of sulphur in metals, in fuels (solid), and in compounds containing higher percentages of sulphur (pyrites, &c.). Many processes may be used for either metals, fuels, or pyrites; these are placed in that connection where they are most commonly used. The arrangement is;—

I. OXIDATION TO SULPHURIC ACID, WITH—

- (a). Gravimetric Estimation.
- (b). Volumetric Estimation.

II. EVOLUTION AS SULPHURETTED HYDROGEN, WITH—

- (a). Gravimetric Estimation.
- (b). Volumetric Estimation.

III. MISCELLANEOUS ITEMS.

I. OXIDATION TO SULPHURIC ACID.

I.a. Gravimetric Estimation.—

764. LEFORT (C. N., xix., 132).—One part HCl to three parts HNO₃ is the most suitable proportion of these acids for the rapid oxidation of sulphur.
765. NICKLES (C. N., vii., 87).—The iron is dissolved in bromine; the S precipitated as BaSO₄.
766. TOSH (C. N., xvi., 168).—Dissolve in HNO₃ with a little HCl, evaporate, re-dissolve in HCl, and add BaCl₂.
767. EGGERTZ (C. N., xvii., 207).—To solution of KClO₃ containing the iron, add HCl, evaporate, filter, and add BaCl₂ to nearly neutral solution. A similar process for iron minerals containing either Ba, Sr, or Pb.
768. PIESSE (C. N., xxviii., 248).—Dissolve in aqua regia, evaporate nearly dry, take up in HCl, and add BaCl₂. WILLIAMS (C. N., xxviii., 266).—Same process, but dissolves in 1:20 HNO₃.
769. ALLEN (C. N., xxix., 91 and 112).—HCl retards, if it does not altogether prevent, the precipitation of BaSO₄; neutralise the iron solution as far as possible with ammonia, and put aside for twenty-four hours. (See 773).
770. PLATZ (Z. I. S. I., 1887, i., 471).—Dissolve in 1:18 HNO₃, evaporate with HCl, &c. The BaSO₄ and wet filter are ignited at low temperature, and then more strongly to oxidise any sulphide to sulphate. (See 786).
771. REIS (Z. I. S. I., 1889, ii., 479).—When iron is dissolved in HNO₃, sulphur escapes estimation as H₂S and S. (See 862).
772. PARRY and MORGAN (C. N., lxvii., 247).—Dissolve in aqua regia, evaporate three or four times with HCl to expel HNO₃, dilute faintly HCl solution to 700 c.c., and add BaCl₂. BaSO₄ is soluble in acid Fe₂Cl₆. Or evolve as H₂S, absorb in CuSO₄, and

ignite precipitate to CuO (see 885). S may be retained by the H₂SO₄ liquor and the insoluble residue.

773. ARCHBUTT (Z. S. C. I., 1890, 25).—In the aqua regia process, BaSO₄ should be precipitated from the concentrated solution; precipitation is complete in two hours, and excess of HCl does no harm (see 841).
774. ANON. (Z. I. S. I., 1893, i., 410).—The nitro-hydrochloric process is subject to error, through formation of basic salts before filtering off SiO₂ or during precipitation of BaSO₄, and precipitating BaSO₄ from too acid a solution.
775. BAMBER (Z. I. S. I., 1894, i., 319).—Dissolve metal in HNO₃, add Na₂CO₃ short of alkalinity, evaporate, roast, extract with dilute Na₂CO₃, and precipitate as BaSO₄.
776. PHILLIPS (C. N., lxii., 239).—S in Cu is estimated by precipitating as BaSO₄ from CuCl₂ solution; BaSO₄ is soluble in Cu(NO₃)₂. Precautions taken against contamination of the BaSO₄ with AgCl or PbSO₄.
777. BRUYN (Z. C. S., lxii., 753) and HEATH (Z. S. C. I., 1896, 218).—Dissolve Cu in HNO₃, precipitate electrolytically, and estimate S in the Cu-free liquor.
778. HAMPE (Z. S. C. I., 1891, 486).—Estimate S in Pb by adding filings to molten KNO₃, passing CO₂ through water solution to precipitate Pb, and adding BaNO₃ to the filtrate.
779. CAMPBELL (C. N., lvi., 74).—Boil soluble slag with HCl and Br, and precipitate nearly neutralised filtrate with BaCl₂.
780. ATKINSON (Z. I. S. I., 1896, ii., 207).—Roast powdered ore, short of fusion, with Na₂CO₃, raising the temperature gradually, dissolve out Na₂SO₄, and precipitate as BaSO₄.
781. PHILLIPS (C. N., lxxv., 194).—By fusion of powdered irons with Na₂O₂ a higher percentage is obtained than by oxidation with acids. The interference of organic sulphur compounds with evolution processes.
782. MEINECKE (C. N., lix., 107), BOUCHER (C. N., lxxiv., 76), and CARNOT and GOUTAL (Z. C. S., lxxii., ii., 520).—Decompose Fe with acid cuprammonium chloride at boiling-point, oxidise filtered residue with aqua regia and KClO₃ or Br and HCl, and precipitate as BaSO₄.
783. TAMM (Z. I. S. I., 1887, ii., 369).—On account of solubility of BaSO₄ in Fe₂Cl₆, add BaCl₂, evaporate, fuse impure BaSO₄ with Na₂CO₃, and reprecipitate. Wiborgh's (925) is more accurate than Eggert's (922) colour process.
784. REIS (Z. I. S. I., 1889, i., 396).—Heat metal with MgO and NaHO, leach, filter, and boil with BaCl₂.
785. MEINECKE (Z. C. S., lxxvi., ii., 518).—Dissolve the pig in HCl and KClO₃; expel Cl, reduce Fe with Zn, and add BaCl₂.
786. BOUSSINGAULT (C. N., xv., 324).—BaSO₄ (CaSO₄, PbSO₄, &c.) is decomposed at high temperatures, and therefore should not be unduly heated.
787. MARSH (C. N., lix., 309).—Appreciable amounts of BaSO₄ are reduced by the carbon of the filter-paper. Precipitate should be treated with H₂SO₄, and again ignited.
788. RIPPER (Z. C. S., lxiv., ii., 239).—Oxidises sulphate reduced by the paper with H₂SO₄ and Br, and removes other impurities by digesting with HCl and Br (see 880).
789. MARBOUTIN (C. N., lxxvi., 232).—By igniting BaSO₄ filter apex upwards no sulphides are formed.
790. FOULK (Z. C. S., lxxii., 189).—Acid solutions need an excess of BaCl₂ to completely precipitate the S. The moist filter is ignited apex up.
791. SLEEPER (C. N., lxix., 63).—BaSO₄ does not carry SiO₂ down with it. SiO₂ can be volatilised from BaSO₄ if free H₂SO₄ is present also.

792. RICHARDS and PARKER (C. N., lxxii., 281).—The occlusion of BaCl_2 by BaSO_4 increases with concentration and the presence of HCl . Results corrected by estimating Cl in the precipitate and deducting equivalent amount of BaCl_2 .
793. SLOANE (C. N., xlv., 221).—The various means of purifying BaSO_4 precipitates, and objections to them.
794. ZIEGLER (Z. I. S. I., 1882, 384).—Add AgNO_3 after BaCl_2 to facilitate and complete the precipitation of BaSO_4 ; wash filter with AmHO to remove AgCl .
795. JANNASCH and RICHARDS (C. N., lx., 19).— BaSO_4 is insoluble in cold ferric solutions. A portion of the iron is always precipitated as barium-ferric sulphate [Schneider, (Z. I. S. I., 1893, i., 409) disputes this], which is decomposed with loss of SO_3 on ignition. Organic acid does not prevent this contamination (see 803 and 846, and Richards, C. N., lxxii., 185).
796. AULICH (Z. I. S. I., 1899, ii., 486).—Resumé of the processes for preventing contamination of BaSO_4 with Fe .
797. MEINECKE (Z. I. S. I., 1899, ii., 490) and HEIDENREICH (Z. C. S., lxxvi., ii., 517).—To prevent iron accompanying BaSO_4 , reduce to FeO with zinc before precipitating.
798. HERTING (Z. C. S., lxxvi., ii., 804).—Reduce to FeO with SnCl_2 before adding BaCl_2 .
799. FRESSENIUS and HINTZ (C. N., lxxiii., 276).—Particulars of the solubility of BaSO_4 with excess of BaCl_2 or H_2SO_4 in water, alkaline chloride, HCl , and HNO_3 solutions.
800. MORGAN (C. N., lviii., 63 and 75).—Reviews some well known objections to the methods based on oxidation and precipitation as BaSO_4 and evolution as H_2S .
801. SPILLER (C. N., x., 219).—Glacial H_3PO_4 and pyrophosphate interfere with the precipitation of BaSO_4 .
802. CROSSLEY (C. N., v., 245).—When S is oxidised by evaporation with HNO_3 an alkaline salt must be added to prevent SO_3 being volatilised.
- 802a. J. T. (C. N., lxxviii., 294).—The blank of the acids used should be found by treating two samples (one half the weight of the other) in the usual way, and deducting the BaSO_4 of the larger from twice the BaSO_4 of the smaller sample.

(To be continued).

THE SPECTRUM ANALYSIS OF NEODYMIUM AND PRASEODYMIUM.

By W. MUTHMANN and L. STÜTZEL.

THE authors first discuss the question as to whether neodymium and praseodymium are really simple bodies, but without giving any definite opinion.

If these elements are provisionally looked upon as undecomposable, it must be remarked that their absorption spectra vary considerably with the dilution, and, above all, with the nature of the acid present. The results are particularly striking if we compare the spectra of the chlorides or the nitrates with those of the carboxylised acetates, lactates, or double alkaline carbonates: the spectra become unrecognisable from one series to the other. Thus, while the solution of chloride of neodymium is red, that of the double potassic carbonate is distinctly blue, and the absorption bands are entirely displaced. The authors have also made estimations of neodymium and praseodymium by examining the absorption bands of various solutions by means of Vierordt's spectro-photometric method; the concentration, c , is related to the intensity I of a band, A being a constant, by the equation $c = \frac{A}{\log I}$.

The agreement with chemical estimations is very satisfactory, especially for strengths of 2 to 6 per cent.

The application of this method to the analysis of didymiferous minerals of different kinds and sources, shows the curious fact that neodymium is always present in practically double the amount of praseodymium.—*Berichte*, vol. xxxii., p. 2653.

THE

PRECIPITATION AND SEPARATION OF COPPER IN ALKALINE SODIC SOLUTION BY MEANS OF SULPHATE OR HYDROCHLORATE OF HYDRAZINE.

By PAUL JANNASCH and K. BIEDERMANN.

ONE of the writers has already been engaged with the quantitative precipitation of copper in the presence of large quantities of caustic soda or potash, with the object of applying it to a certain number of metallic separations. Up to the present time this has only been effected quantitatively with metals whose hyperoxides (peroxide of hydrogen method), or hydroxides are insoluble in an excess of soda. Such, for instance, is the case in the separation of arsenic, associated with manganese or iron (Jannasch, *Praktischer Leitfaden d. Gewichtsanalyse*, 65). This, however, is no longer the case with oxide of copper, which is slightly soluble in caustic soda. When we have to do with this metal, it is necessary, for accurate work, to get rid of the excess of alkali after precipitation.

The first exact experiments, carried out by one of the writers in collaboration with H. Winkler, were based on the use of hydroxylamine, which precipitates the whole of the copper in the state of cuprous oxide in strongly alkaline solutions. After having overcome several technical difficulties connected with the filtration of the precipitate, and the prevention of partial re-oxidation, the above mentioned chemists succeeded in obtaining good results, both in the estimation of copper alone and in the separation of this metal from zinc and arsenic.

As for the difficulties mentioned above, the authors of this present paper have entirely removed them by replacing the hydroxylamine with hydrazine of Curtius, who kindly placed some sulphate at their disposal.

I. Determination of Copper.

The quantitative precipitation of this metal is effected in alkaline solution in the presence of sulphate of hydrazine. To effect the estimation, we take an accurately weighed quantity of cupric sulphate and dissolve it in a beaker with a little warm water. The solution thus prepared is then run into a porcelain crucible containing pure soda lye (5 grms. NaOH : 50 c.c. H_2O). As the copper salt is added in the cold, a pale blue precipitate of hydrate of copper is first formed. At this moment a boiling solution of 3 per cent sulphate of hydrazine (1—2 c.c.) is added, and the whole then gently heated on the water-bath with continual stirring. There is an immediate disengagement of gas, and the formation of protoxide of copper, which, after the addition of a further quantity of the solution of hydrazine (about 3 c.c.), is converted into metallic copper. This latter is quickly deposited at the bottom of the beaker. It is necessary to allow the liquid to cool, or to dilute it with water before filtration, to prevent the alkali from attacking the paper. We may further make use of two filter-papers with advantage, having the interior one about a couple of centimetres shorter than the other; by this means we can prevent small particles of the substance from passing over the edge of the paper during the washing. The precipitate must be washed with warm water until the washings no longer react on litmus, and leave no residue when evaporated to dryness on a strip of platinum foil. It is then dried at 90° , the filter calcined apart in a tared porcelain crucible, and after having added the rest of the

precipitate, the whole is heated to redness in a current of oxygen. This latter condition is not absolutely necessary if we take care to stir the material with a platinum spatula so that every part of it may come in contact with the air. The calcination is continued until the weight is constant, and as a further precaution, we make sure that the transformation into cupric oxide is complete by treating the product of incineration with a few drops of concentrated nitric acid. The authors have from time to time made a control calcination in oxygen.

First Analysis.—0.2218 grm. $\text{CuSO}_4 + 5\text{H}_2\text{O}$: 0.0704 grm. CuO =0.0562 grm. Cu =25.29 per cent (theory = 25.42 per cent).

Second Analysis.—0.2094 grm. $\text{CuSO}_4 + 5\text{H}_2\text{O}$: 0.0666 grm. CuO =0.0532 grm. Cu =25.41 per cent (theory = 25.42 per cent).

II. Separation of Copper and Zinc.

The salts employed for this separation were sulphate of zinc and sulphate of copper, of which the aqueous solution was poured drop by drop into a vessel containing 10 per cent soda-lye. The use of glass must be avoided, as it resists the action of the alkaline solution of hydrazine very badly, thus causing the formation of impurities whose presence would interfere with the accuracy of the estimation. In some experiments even platinum crucibles were found to be unsuitable, as they often permitted particles of precipitated copper to adhere to their sides.

We then add 5 c.c. of a 3 per cent solution of hydrazine to the cold, strongly alkaline liquor, and heat carefully with continual stirring. After a few minutes the copper is completely precipitated in the state of a reddish-brown precipitate, which is treated in the manner described above. After prolonged washing with warm water, the last traces of hydrate of zinc can be removed by treating with very dilute, warm caustic soda. The authors, however, have hardly ever found this kind of impurity in the numerous estimations they have carried out. The copper, dried at 60°, is then calcined in a porcelain crucible until the weight is constant. It is necessary, as has been explained in the case of the estimation of copper alone, to disaggregate the mass with a platinum spatula. This operation may in the same way be replaced by treatment with oxygen or concentrated nitric acid.

As for the solution containing the zinc it is treated with hydrochloric acid until the precipitate first formed is redissolved, and the colourless liquid has a distinct acid reaction. We then add excess of a solution of carbonate of soda, stirring the whole time. To prevent loss by projection the beaker is covered with a watch-glass with a hole to allow the passage of the stirring rod. The carbonate of zinc is then converted into oxide by calcination, and this, if it does not contain any trace of silica, should be absolutely white, and should give a clear limpid solution with dilute acetic acid.

First Analysis.—0.2940 grm. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ +0.1525 grm. $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ =0.4465 grm. substance; 0.0935 grm. CuO =0.0746 grm. Cu =16.73 per cent (theory = 16.77 per cent); and 0.0431 grm. ZnO =0.3430 grm. Zn =7.68 per cent (theory = 7.74 per cent).

Second Analysis.—0.3040 grm. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ +0.1890 grm. $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ =0.4930 grm. substance; 0.0949 grm. CuO =0.0770 grm. Cu =15.61 per cent (theory = 15.69 per cent); and 0.0527 grm. ZnO =0.4230 grm. Zn =8.58 per cent (theory = 8.68 per cent).

III. Separation of Copper and Arsenic.

In this case the writers have used cupric sulphate and arsenious acid. This latter was transformed, for the purpose of estimation, into arsenic acid by the aid of a few drops of concentrated nitric acid.

The aqueous solution of the two elements to be separated, was gradually added to 40 or 50 c.c. of 10 pe-

cent soda-lye, and after the addition of 4 or 5 c.c. of the solution of sulphate of hydrazine, the mixture was submitted to the action of heat. In this manner a precipitate of metallic copper is formed which is treated as before.

The arseniate of soda passes into the filtrate, and is in its turn treated in the following manner:—For the purpose of first removing the excess of soda, the alkaline solution is saturated with hydrochloric acid, to which a small quantity of nitric acid is added at the end; the whole is then concentrated down to about 80 c.c. If the solution contains any silica from the glass of the apparatus, it is necessary to saturate with nitric acid, evaporate to dryness, take up the residue with acidulated water, and separate the insoluble impurities by filtration. When the filtrate is quite cool, we add to the clear, colourless solution an excess of ammonia and freshly prepared magnesia mixture. The mixture is then left at the ordinary temperature for fifteen or twenty-four hours, and we can then proceed with the filtration of the ammonio-magnesian arseniate, which is frequently deposited in the form of beautiful well-formed needles. (For further details refer to *Prakt. Leitfaden der Gewichtsanalyse*, p. 64).

First Analysis.—0.1255 grm. As_2O_3 +0.2801 grm. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ =0.4056 grm. substance; 0.1964 grm. $\text{Mg}_2\text{As}_2\text{O}_7$ =0.0948 grm. As =23.37 per cent (theory = 23.41 per cent); and 0.0886 grm. CuO =0.0708 grm. Cu =17.46 per cent (theory = 17.54 per cent).

Second Analysis.—0.2230 grm. As_2O_3 +0.2556 grm. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ =0.4786 grm. substance; 0.3495 grm. $\text{Mg}_2\text{As}_2\text{O}_7$ =0.1687 grm. As =35.24 per cent (theory = 35.29 per cent); and 0.0813 grm. CuO =0.0649 grm. Cu =13.56 per cent (theory = 13.68 per cent).

IV. Separation of Copper and Tin.

As the result of a long series of experiments and more than thirty estimations, the authors have succeeded in finding a practicable and exact method for the separation of these two metals. They used a mixture of pure copper and pure tin, which they dissolved in the quantity of aqua regia necessary to obtain a bright green solution. If an excess of these acids has been used it is necessary to get rid of it after the solution is complete, by means of careful evaporation. The solution diluted with water is then poured drop by drop into a solution of caustic soda containing 15 times the weight of alkali that there is of metal present, and to which 2 or 3 grms. of hydrochlorate of hydrazine have been added. The action of this latter salt is identical with that of the sulphate used in the preceding operations. However, after having made numerous separations of copper and tin the authors have come to the conclusion that the presence of sulphates interferes with the accuracy of the analysis. In fact, in such a case the copper always contains traces of tin which are impossible to remove by washing with warm dilute soda, and which therefore make the amount of copper found too high.

The precipitated copper is heated for some time in a porcelain crucible in the presence of excess of hydrazine so as to dissolve the small quantity of tin which has escaped the action of the alkali in the state of sodic stannate. After cooling and diluting the liquid, the precipitate is thrown on a double filter and carefully washed with boiling water. The rest of the treatment is the same as with the previous separations.

The alkaline solution containing the tin is then treated with a slight excess of concentrated hydrochloric acid and saturated with ammonia. This latter causes the precipitation of the stannous hydrate which is re-dissolved in sulphide of ammonium. This new solution is then heated for some time on the water-bath, and made slightly acid with dilute hydrochloric acid. The sulphide of tin which is deposited by this means is filtered, washed with a warm solution of sulphuretted hydrogen, and transformed into stannic acid by calcination in a current of oxygen.

First Analysis.—0.0813 grm. Cu + 0.2336 grm. Sn = 0.3149 grm. substance; 0.1014 grm. CuO = 0.0810 grm. Cu = 25.72 per cent (theory = 25.81 per cent); and 0.2965 grm. SnO₂ = 0.2332 grm. Sn = 74.06 per cent (theory = 74.18 per cent).

Second Analysis.—0.1247 grm. Cu + 0.2729 grm. Sn = 0.3976 grm. substance; 0.1558 grm. CuO = 0.1244 grm. Cu = 31.28 per cent (theory = 31.38 per cent); and 0.3461 grm. SnO₂ = 0.2732 grm. Sn = 68.48 per cent (theory = 68.61 per cent).

—*Berichte*, vol. xxxiii. p. 631.

FURTHER EXAMINATION OF THE SOLUBILITY OF LIME IN SACCHARINE SOLUTIONS.

By J. WEISBERG.

I. The Solubility of Lime in its Different Forms, in Saccharine Solutions at the Ordinary Temperature.

In a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 773) we examined the solubility of powdered calcic oxide (CaO) in solutions of sugar at a temperature of 15–16°, and showed that this solubility is much greater than has been observed by other chemists who have already studied this question. But, as far as the extreme limit of saturation of the saccharine solutions experimented on is concerned, we added that we could not guarantee having absolutely reached it in our experiments. To attain the maximum limit of saturation, it is necessary to operate with a very large excess of lime compared with the amount which could be actually dissolved.

We now complete our previous research on this subject, by considering in this paper not only the solubility of the dry, powdered, calcic oxide, but also that of hydrate of lime, Ca(OH)₂, and of milk of lime.

To determine the comparative solubility of lime in its three different forms which are in practical use, the quantities of material added in excess in the three different cases were kept as nearly as possible in the same proportions. The saccharine solutions experimented upon were treated with practically identical quantities of lime in its three different forms; the stoppered flasks containing the sucro-calcic mixtures were left, with occasional agitation, as long as was necessary to obtain filtered solutions of constant composition. The temperature at which we carried out these experiments varied only between very narrow limits (15–16°). All the results of these comparative experiments are given in Table I. in full detail. The figures in that table show:—

1. That the solubility of lime in its three forms, in saccharine solutions of known strength and at a temperature of 15–16°, is much greater than has been recorded by previous observers.

2. That, under the same experimental conditions, oxide of calcium is the most soluble, followed by hydrate of lime and then by milk of lime, in which form the relative solubility of lime is the weakest.

As far as concerns oxide of calcium, its solubility in saccharine solutions of medium concentration is about 28 parts of CaO for every 100 parts of sugar in solution; but this solubility, although great, does not yet represent the extreme limit, for, on different occasions, we have prepared sucro-calcic solutions in which we have estimated the presence of 28.5, 29.0, 29.5, and even 30.5 (the extreme limit) parts of CaO for each 100 parts of sugar in solution, and that, in solutions the concentration of which varied between 8 and 17 per cent of sugar, using powdered calcined marble, or again, a well-burnt lime from a very pure commercial carbonate of lime, and at a temperature of 15–16°.

If our table does not contain these figures of high solubility, it is because we did not admit any but *stable sucro-*

calcic solutions—that is to say, solutions which remained clear even when the temperature was lowered several degrees relatively to that at which their composition was determined. The sucro-calcic solutions containing 28.5 to 30 parts of CaO for each 100 parts of sugar (saccharine solutions containing 10 to 16 per cent of sugar), at a temperature of 16°, do not always remain limpid when left at a temperature lower than that we have mentioned; they often give a deposit more or less voluminous, and on separating the supernatant liquid from the deposit we find in the filtrate a quantity of dissolved lime equivalent to that given in the table (27 to 28).

All the sucro-calcic solutions experimented upon, when heated on the water-bath, became cloudy, gave a deposit, and, according to the concentration, became gelatinous, but the deposit formed during the heating was re-dissolved on cooling, and the solutions became clear and limpid again. The more lime the liquid contained, the sooner the gelatinous precipitate commenced to form on heating. Of two saturated saccharine solutions of lime, heated simultaneously on the water-bath, it is the solution which has its lime in the form of oxide of calcium which becomes cloudy first, while the other sucro-calcic solution which has its lime in the form of hydrate, or of milk of lime, does not become cloudy until a little later, when the temperature has increased to several degrees higher than the first one. Suro-calcic solutions of medium concentration (containing 10 to 16 per cent of sugar and 27 to 28 parts of lime for each 100 parts of sugar in solution), when heated in a test-tube on the water-bath, first become cloudy, and then form a white paste sufficiently solid for the tube to be turned upside down without any material falling out.* On cooling, the paste becomes liquid again, and the solution is as clear and limpid as before heating.

II. On the Solubility of Lime in Saccharine Solutions at a High Temperature.

Dubrunfaut (*Comptes Rendus*, xxxii., p. 498) and Lippmann (*Chemie der Zuckerarten*, p. 620), first observed that the solubility of lime in solutions of sugar, as well as in pure water, depends essentially on the temperature; but it is to Lamy (*La Sucrerie Idigène et Coloniale*, vol. xi., p. 234-237), and Lippmann (*Chemie der Zuckerarten*, p. 650), that we owe a series of determinations of the solubility of lime in a 10 per cent saccharine solution, at different temperatures, which determinations were given by him in a Report presented in 1876 to the Société Industrielle du Nord.

Lamy endeavoured to determine the amount of CaO which could be dissolved at 30°, 50°, 70°, and 100°, by 100 parts of a decinormal solution of sugar when 1 or 2 per cent of its weight of lime was added. Slaked lime, mixed with the saccharine solutions at the temperature of the experiment, was left for three hours with frequent stirring; the temperature was then raised, and the solution filtered rapidly. Table II. gives the figures found by Lamy for

* In principle, the few reactions we have mentioned in the preceding lines, and which take only a secondary place in this article (as its title shows), are not quite new, and we do not offer them as such. They are mentioned because we have experimented with a large number of monocalcic solutions—all solutions which are included in our tables of the solubility of lime already published, and which we now publish in this article. In this manner we have, independently of our predecessors (Payen), prepared a complete series of sucro-calcic solutions, which, on being heated to 90–95°, become quite solid. It is very simple to prepare saturated sucro-calcic solutions which form a thick paste on being heated to the above-given temperature, while up to the present only a single special receipt had been given for producing this characteristic reaction, which is occasioned, according to some chemists, by the precipitation of a hexacalcic sucrate (?), the existence of which is far from having been proved. On the other hand, we read on page 763 of M. von Lippmann's book, entitled *Chemie der Zuckerarten*, as follows:—"By dissolving the calcic monosucrate in 4 parts of water, and boiling the solution obtained, a thick paste is formed which can be turned upside down in the beaker, without any loss." These few remarks will make clear the difference, or the analogy, between our own observations and those of our predecessors in this subject.

TABLE I.—Comparative Results of the Solubility of Calcic Oxide, Hydrate of Calcium, and Milk of Lime in Saccharine Solutions at a Temperature of 15–16°.

Powdered oxide of lime, CaO.			Hydrate of lime, Ca(OH) ₂ .			Milk of lime, Ca(OH) ₂ +aqua.		
Saccharine solution.	Sucro-calcic mixture.	Filtered sucro-calcic solution.	Saccharine solution.	Sucro-calcic mixture.	Filtered sucro-calcic solution.	Saccharine solution.	Sucro-calcic mixture.	Filtered sucro-calcic solution.
Grms. of sugar per 100 c.c. of solution.	Grms. of CaO per 100 c.c. of mixture before filtration.	Grms. CaO in solution per 100 grms. of sugar.	Grms. of sugar per 100 c.c. of solution.	Grms. of CaO per 100 c.c. of mixture before filtration.	Grms. CaO in solution per 100 grms. of sugar.	Grms. of sugar per 100 c.c. of solution.	Grms. of CaO per 100 c.c. of mixture before filtration.	Grms. CaO in solution per 100 grms. of sugar.
13'00	6'37	27'75	13'00	6'00	25'40	—	—	—
11'34	5'52	27'57	11'96	5'55	25'45	11'18	5'40	22'40
10'30	5'10	27'86	10'87	5'07	25'40	10'04	5'00	22'90
9'67	4'70	27'61	9'67	4'50	25'00	—	—	—
8'27	4'00	27'49	8'90	4'12	24'74	8'68	4'27	22'80
7'64	3'55	27'50	8'06	3'72	24'72	7'28	3'80	21'70
6'84	3'32	27'42	6'97	3'32	24'50	6'29	3'20	20'90
5'77	2'60	27'80	5'46	2'60	24'50	5'22	2'72	20'55
4'73	2'17	27'90	4'52	2'25	24'23	4'03	2'18	20'60
3'95	1'70	27'73	3'56	1'63	23'60	—	—	—
3'02	1'23	27'78	2'57	1'30	23'40	—	—	—
2'29	0'92	27'93	1'85	0'88	23'30	2'91	1'54	20'05

TABLE III.—Solubility of Lime, in Three different Forms, in Saccharine Solutions at Temperatures of 80° and 90°.

Dry powdered lime, CaO.				Hydrate of lime, Ca(OH) ₂ .				Milk of lime, Ca(OH) ₂ +aqua.			
Composition of the sucro-calcic solution at the ordinary temperature.		Composition of the same solution heated to 80° and filtered at the same temperature.		Composition of the sucro-calcic solution at the ordinary temperature.		Composition of the same solution heated to 90° and filtered at the same temperature.		Composition of the sucro-calcic solution at the ordinary temperature.		Composition of the same solution heated to 90° and filtered at the same temperature.	
Grms. of sugar per 100 c.c. of solution.	Grms. of CaO in solution per 100 grms. of sugar.	Grms. of sugar per 100 c.c. of solution.	Grms. of CaO in solution per 100 grms. of sugar.	Grms. of sugar per 100 c.c. of solution.	Grms. of CaO in solution per 100 grms. of sugar.	Grms. of sugar per 100 c.c. of solution.	Grms. of CaO in solution per 100 grms. of sugar.	Grms. of sugar per 100 c.c. of solution.	Grms. of CaO in solution per 100 grms. of sugar.	Grms. of sugar per 100 c.c. of solution.	Grms. of CaO in solution per 100 grms. of sugar.
13'68	27'8	10'97	21'18	12'63	25'5	8'16	7'50	—	—	—	—
10'76	27'6	7'49	16'60	11'59	26'0	7'12	6'84	11'49	23'1	8'79	11'79
8'66	27'7	4'58	16'15	9'15	26'0	5'72	6'36	8'85	23'1	6'29	8'18
4'00	27'4	2'68	13'59	8'68	25'5	5'62	7'67	5'67	23'1	3'95	7'65
4'43	27'8	2'78	8'85*	—	—	—	—	—	—	—	—

* Heated to 90° instead of 80°.

the solubility of lime in saccharine solutions at 10 per cent, using 2 grms. of lime per 100 grms. of sugar solution.

TABLE II.—Lamy's Table.

Temperature.	CaO dissolved in 10,000 grms. of decinormal sugar solution.	CaO dissolved in 10,000 grms. of pure water.	Difference, expressing the lime united with the sugar.
100°	15'5	6'0	9'5
70°	23'0	7'9	15'1
50°	53'0	9'6	43'4
30°	120'5	11'7	108'3

We have also made a certain number of experiments for estimating the solubility of lime in saccharine solutions at high temperatures, but we may remark that we do not consider the results yet obtained as completely trustworthy.

We operated in a different manner to that adopted by Lamy. Clear sucro-calcic solutions, saturated with lime at the ordinary temperature, were heated on the water-bath to the temperature mentioned later on. The gelatinous deposit formed was separated from the liquid portion by rapid filtration through a filter kept heated to the same temperature. The liquids separated from the deposits were then cooled to the ordinary temperature, and analysed.

The accompanying Table III. shows the composition of the sucro-calcic solutions before and after heating.

The figures of this table show that, under the conditions of our experiments, the solubility of lime, even at 80° and 90°, is still considerable—much greater, in fact, than that found by Lamy.—*Bull. Soc. Chim.*, Series 3, vol. xxiii., No. 18.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF SILVER.*

By LAUNCELOT W. ANDREWS.

THE chief volumetric methods now in use for silver determinations are those of Gay-Lussac (G. J. Mulder, *Scheikundige verhandelingen*, 1857), Pisani (*Ann. des Mines*, [5], 10-83), Mohr ("Titrimethode," 3rd ed., § 151), and Volhard (*Ann. Chem.*, Liebig, cxc., i).

Of these, the first, as is well known, is a process of great accuracy, applicable to acid solutions, but is tedious in execution. The second and third are only to be used in perfectly neutral solutions, so that their application is extremely limited, being excluded in those cases where neutralisation produces a precipitate. The method of Volhard is free from these drawbacks, but is seriously interfered with by the presence of substances which impart a yellow or red colour (such as cobalt salts) to the solution, and for those cases in which the amount of silver is extremely small or the solution highly dilute it lacks the sensitiveness of the methods of Gay-Lussac or Pisani, probably because the reaction between sulphocyanates and ferric salts is less delicate as a test for the former than for the latter.

It has therefore appeared to the author to be a matter of some interest to devise a method applicable to acid solutions containing silver along with a variety of other metals, possessing the delicacy characteristic of the starch.

* Presented at the New York Meeting of the American Association for the Advancement of Science, June 28, 1900. From the *American Chemical Journal*, vol. xxiv., No. 3.

iodide reaction. It is the purpose of this paper to present such a method, based upon that of Pisani.

In Pisani's method, a solution of starch iodide is run into the silver solution containing calcium carbonate in suspension.

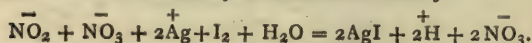
The exact nature of the reaction which then occurs, and which culminates in decolorisation of the iodide of starch, has not been as yet cleared up in spite of several investigations which have been published on the subject. Silver iodide is precipitated along with oxidised products, silver iodate, hypoiodite, or, possibly, silver peroxide in the latter stages of the reaction. Strict proportionality does not exist between the amount of starch iodide consumed and the silver present, although such proportionality is more nearly approached as the solution used is more dilute. The departure from proportionality for solutions between N/100 and N/200 is considerable, as the following experiments show.

In each experiment 25 c.c. of a solution containing 0.7887 m.grm. of silver per c.c. was employed, and the quantity of water added was varied. The results of one set of observations are subjoined.

Expt. No.	Vol. of water added in c.c.	Vol. of Pisani's sol. required.	Character of end reaction.
		C.c.	
41	None	15.70	Obscure, colour dirty.
42	300	18.60	Sharper.
43	None	15.40	As in No. 41.
44	500	20.25	{ Sharp, change from brownish to blue.
45	300	18.70	As in No. 42.

If the effort is made to titrate a silver solution acidified with nitric acid by one of starch iodide, a series of colours may be observed, beginning with yellow and passing through orange, brown, grey, sage-green, &c., without any turning-point being clearly marked.

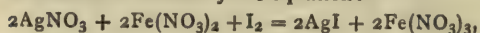
During these changes, the solution exhibits powerfully oxidising properties, more marked than are shown by dilute solutions of either iodine or of iodic acid. The reaction between free iodine and solutions of silver nitrate is now under investigation at this laboratory, and the author hopes to publish definite results before long; in the meantime it will suffice to say that the following general reaction is probable, the equation being written in the sense of the electrolytic dissociation theory:—



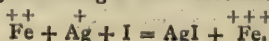
Here the iodine plays a part similar to that which it holds in iodine monochloride and the—for the present—hypothetical compound INO_3 is to be regarded as the carrier of the oxidising properties referred to above. It exerts the oxidising action upon organic matter present (as starch), and upon any other reducing substances such as ferrous salts, nitrous acid, or tetrathionates. It undergoes in part hydrolysis into HOI and nitric acid, and in part reacts with the excess of silver nitrate, producing a reddish-brown solution precisely similar in appearance and properties to that obtained by dissolving "silver peroxide" in nitric acid (J. Fischer, *J. Prakt. Chem.*, xxxiii., 237), and which presumably contains silver pernitrate.

In place of these complicated reactions, a simple one ensues if from the start a sufficient quantity of a feeble reducing agent is present, as ferrous salt or nitrous acid, of such character as not to react with free iodine or starch iodide. In that case a smaller quantity of the solution of iodide of starch will be required than if the titration were conducted according to Pisani in neutral solution, and the end of the reaction is marked by a sharp change from pale yellow to blue.

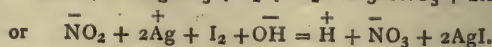
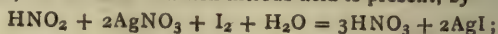
The reaction is shown by the equation:—



or more simply according to the dissociation theory:—



and, for the case in which nitrous acid is present, by—



As might be expected from the respective equations, the reaction in the presence of ferrous salts is practically instantaneous, while that which takes place in the presence of nitrous acid is much slower, especially in very dilute solutions, owing to the slight dissociation of the water and consequent small number of hydroxyl ions that are directly involved in the reaction.

Dilute solutions of ferrous salts, slightly acidified by strong acids, will very slowly decolourise properly prepared starch iodide, with the formation of traces of ferric salts. This action can be checked by the previous addition of ferric salt. Thus, if 2 c.c. of a solution of 40 grms. of crystallised ferrous ammonium sulphate in a litre of water be added to 100 c.c. of water containing 5 c.c. of dilute nitric acid, and a few drops of N/1000 starch iodide then run in to colour the liquid blue, spontaneous bleaching will ensue in about five minutes, whereas, if the iron solution also contain 40 grms. of ferric ammonium sulphate (cryst.) per litre, five to eight hours will elapse before the blue disappears. That there is a condition of equilibrium between ferrous and ferric salts and iodine and iodide, has been shown by Seubert and Dörner (*Ztschr. Anorg. Chem.*, v., 339-411), and by Seubert and Rohrer (*loc. cit.*, vii., 137).

In applying the facts just set forth to the development of a practical volumetric method, the slight solubility of silver sulphate must be borne in mind. If the iron sulphate is added to a too concentrated silver solution, and then titration with starch iodide is undertaken, silver sulphate will be thrown down with silver iodide, and partly enveloped by the latter, making the end-point obscure and the results more or less inaccurate. Some of the experiments described in the following portion of this paper give evidence of this fact and also show the permissible limits of concentration.

Before describing in detail the analytical method, it will be well to say a word regarding the adjustment of apparatus and the preparation of solutions employed.

Apparatus.

All burettes and other pieces of volumetric apparatus employed in the work were carefully calibrated and the readings corrected to true cubic centimetres. The burettes were divided into 1/10 c.c., with divisions sufficiently wide to permit 1/100 c.c. to be estimated with an error of not more than 2/100 c.c. The solution of iodide of starch in the concentrations used is almost perfectly opaque, and permits very exact readings to be taken from the top of the meniscus, which method was uniformly used.* Pipettes and burettes were frequently cleaned with a strongly alkaline solution of potassium permanganate followed by hydrochloric acid, a method to be recommended in preference to that involving the use of sulphuric acid and potassium bichromate commonly employed.

Preparation of Standard N/10 Silver Solution.

Commercial "pure silver 1000 fine" was dissolved in pure nitric acid and water, heated in porcelain, and filtered. An excess of the purest hydrochloric acid was added, and stirring continued until the precipitated chloride had become granular. The precipitate, after being thoroughly washed by decantation, was reduced by digestion on the steam-bath with formaldehyde and ammonia. The silver sponge so obtained was washed with distilled water, compressed and fused in an unglazed porcelain crucible without flux, cast in an ingot mould, treated with fusing caustic

* The use of a float is not to be recommended, according to the author's experience, for either opaque or transparent liquids. Many series of readings made with and without this device, the results being controlled by weighing the liquid delivered, have shown that the float increases instead of diminishing the probable error of a reading, provided the readings are taken in the proper way when no float is used; i. e., with suitable illumination.

potash, and finally cleaned mechanically. The N/10 solution was made up to contain 10.793 grms. (corrected) of this silver per true litre. From this standard a N/100 solution was prepared directly by dilution, and for some of the experiments, other, less pure, silver solutions were standardised by comparison.

Preparation of the Starch Iodide.

The best obtainable commercial maize starch was repeatedly washed with water by decantation, strained through linen, washed with dilute hydrochloric acid, then with pure dilute caustic potash, again with hydrochloric acid, then in turn with water, alcohol, ether, and finally alcohol, and dried at 40°. This purification is not essential, but the starch employed had been purified in this way for the purposes of a correlated research on the properties of starch iodide.

Of the prepared starch, 50 grms. were ground dry with 8 or 9 grms. of re-sublimed iodine until well incorporated, and the powder stirred with 100 c.c. of distilled water, sealed up in large glass tubes, and heated for several hours in boiling water. Instead of heating in sealed tubes, boiling with water in a flask with reflux condenser may be equally well employed, the iodine, which at first sublimes into the condenser, being pushed back into the liquid from time to time. The substance obtained in either way, after moderate dilution, is filtered through a "toughened" (parchmentised) filter. Solution is complete. N/20 standard solutions were made, but N/100 is as far as it is convenient to go in concentration usually. These solutions are as absolutely permanent as any volumetric solutions can be, changing in strength only by evaporation of water. By blowing a current of air through such a solution for a day or two the vapour-pressure of the iodine can be reduced to 0.005 m.m., and even less, as was determined by a method to be published elsewhere.

For all titrations where an iodine solution weaker than N/20 is to be used, as in the titration of alkaline arsenites, antimonous salts, &c., iodide of starch solutions are to be preferred to those prepared in the ordinary way from potassium iodide and iodine, since the former are more permanent, give an even sharper end-reaction, can be more exactly read off in the burette, and avoid the difficulty of preparing a clear, permanent starch solution as indicator or the trouble of always making up a fresh one. The standard of a solution of starch iodide as regards silver is not the same as its standard toward sodium thiosulphate, since only a part (often about two-thirds) of its iodine is in a condition to react with reducing agents, the remainder being in a form analogous to an alkyl iodide, reactive toward silver salts but not toward thiosulphates, and the like.* In some experiments (referred to below) a N/10 solution was prepared (designated "Sol. A") by mixing about 600 c.c. of N/50 starch iodide with about 400 c.c. of ordinary decinormal iodine solution. The mixture was decinormal as regards total iodine. Such solutions can be used when larger amounts of silver are to be titrated, but I believe it to be better in such cases to precipitate the greater part of the silver with a N/10 potassium iodide solution and finish with the N/100 starch iodide, or to use a N/10 potassium bromide, and then, after filtration, to titrate with the starch iodide. Starch iodide reacts with the chloride, bromide, cyanide, or sulphocyanate of silver, so that these salts must always be filtered out before proceeding to the residual titration.

Auxiliary Solutions.

Iron solution C contained 40 grms. ferrous ammonium sulphate and 40 grms. ferric ammonium sulphate with a few c.c. dilute sulphuric acid to the litre. For reasons already given, it is desirable to have solutions of ferrous and ferric salts free from sulphates to use for this method. Experiments were accordingly made with solutions ob-

tained from iron and dilute nitric acid, containing about 28 grms. of iron to the litre, and were successful. Such solutions have the disadvantage of gradually becoming deep brown, in consequence of the formation of basic ferric nitrate, and they contain organic matter derived from the carbon of the iron. This organic matter takes up a little iodine, and therefore decolourises starch iodide. Solutions prepared from strontium nitrate with solutions of ferrous and ferric sulphates are free from the latter objection, but not entirely from the former.

Instead of ferrous solutions, those of nitrous acid may be employed as previously mentioned. They may suitably be prepared by dissolving 30 grms. of sodium nitrite (free from chloride) in 1 litre of dilute nitric acid (13 per cent). Such a solution is designated "Sol. D" in the accompanying tables.

(To be continued).

ARSENIC IN BEER.

By CHARLES ESTCOURT, F.I.C., F.C.S.,
Public Analyst to the City of Manchester.

THERE is no doubt that substances enter into the composition of modern beer which interfere with the usual methods of analysis for the detection of arsenic. This must have forcibly struck every chemist who has analysed beer for the presence of arsenic—as very many have—in beers brewed from arsenical glucose, and failed to detect it. Two of the nostrums used in the brewing of modern ales are finings (which are "cut" with sulphurous acid) and bisulphites of lime and magnesia, &c. These are both used as preservatives, either in washing the barrels, or by adding direct to the beer. If chemists had been acquainted with the presence of these in beer, much less difficulty would have been felt in dealing with arsenical beer. Both these compounds will prevent the discovery of arsenic in beer by the Marsh test, and by the Reinsch also, for unless the beer is boiled some time with acid before putting in the copper the sulphurous acid in the beer will produce the blackening.

Beers brewed from malt, hops, and glucose may be used direct in the Marsh apparatus, and if arsenic is present it will be detected. I have tried the experiment upon beers before racking when no sulphurous had been added. Thus it is not organic matter alone which makes arsenic in beer so difficult of detection, which I proved by taking a beer absolutely free, and adding to it a known quantity of arsenious acid. In the Marsh apparatus I got out practically all I had introduced. To another portion of the same beer with arsenic in such proportion as gave a large deposit in the heated tube, I added a very small quantity of a bisulphite of calcium, and got no deposit of arsenic on the heated tube, only sulphur appearing there. The arsenic was obtained from the flame at the end of the tube when received on porcelain.

The difficulty in connection with the twelve samples of Manchester beer is now explained. I had to do the samples in a day. I did take twelve working hours, and knowing nothing of the presence of sulphite, I found no arsenic. I may say I had only about 11 ounces per sample, and in the small quantities I used for experiments the trace of arsenic was probably lost in the preparation of the beer for the Marsh test. I may premise that I tried a series of experiments with the original beer.

Any test to succeed must deal with not less than 100 c.c., and this should be charred, *only to intumescence*, with acid, then diluted and filtered, and the filtrate evaporated. I did this process in flasks, but found the Medical Officer here was doing the process in porcelain basins, which I now adopt. If one omits to evaporate the filtrate, sulphurous acid may easily be present (carbonaceous matter and sulphuric acid), and spoil the experiment.

City Laboratory,
St. Andrew's Chambers, 20, Albert Square,
Manchester, December 10, 1900.

* Compare Mylius (*Ber. d. Chem. Ges.*, xx., 658). The statement made above is intended to apply to iodide of starch prepared by the aid of heat, as described in the present paper.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 274).

2. Soluble Selenium.

It is familiar to everyone who has carried out the reduction of selenious acid by sulphurous acid, in solution, that when the two liquids are mixed, there is often no precipitation at first; the colour changes from yellow to a more or less deep red, and only after the lapse of a certain time is a deposit of red selenium formed. This makes its appearance then as a red powder, or as a golden or red translucent skin upon the sides of the vessel.

Schulze (1885) has carried out experiments upon these coloured solutions, and his observations, as far as the solubility of the element is concerned, have been confirmed by Muthmann (1887). Schulze's results point to the existence here of a mono- and perhaps a di-selenium trithionic acid, $\text{H}_2\text{S}_2\text{SeO}_6$ and $\text{H}_2\text{SSe}_2\text{O}_6$. These acids are instable in the presence of mineral acids, and it is perhaps by this breaking down that the red solutions are formed which afterwards deposit amorphous selenium.

Schulze has observed that the red selenium precipitated from such solutions re-dissolves if an excess of water be added, and that it loses this solubility in a short time, especially if exposed to the light. The solution is stable in the dark, but when allowed to stand in the light, deposits selenium in the form of a red film or skin. By dialysis all foreign substances can be removed. The solution may be boiled without decomposition, but the addition of salts and acids throws out the selenium. Selenium in this form has very strong colouring power; solutions of 1 part in 10,000 parts of water are distinctly reddish.

If we assume that this freshly precipitated selenium forms solutions in the ordinary sense of the word, and loses its solubility on standing, we are led to the conclusion that we have here to do with a distinct form of the element. If, on the other hand, we suppose—what is highly probable—that the acids described by Schulze are colourless, and that the solutions owe their colour to selenium in suspension, then it is quite conceivable that the change in the substance on standing is simply one of aggregation, the extremely small particles deposited from suspension clotting together to larger masses incapable of re-solution. This accords very well with the nature of the red powder and with the familiar observation that at 40° — 50° it clots together to a soft sticky mass.

3. Amorphous Selenium.

Even when freshly precipitated selenium is merely suspended in the liquor, it often remains for hours without settling down. If the vessel be laid aside and the precipitate allowed to come down slowly it forms a soft mass in the bottom of the vessel, resembling in texture and mobility a soft coagulated jelly. When shaken, it does not at first go into powder, but breaks along irregular lines. When dried, it forms an impalpable powder which cannot easily be completely removed from any material with which it has come into contact—the hands, filter-paper, &c.

Hittorf (1851) records that the red powder of selenium when subject to the heat of the sun's rays becomes partially crystalline, but this was probably a heating effect, or he may have been deceived by the change of colour. I have repeated the experiment, and find that there is a rapid change in colour, but the product appears to be still the amorphous form, though much darkened and clotted together.

When gradually warmed, the powder begins to be somewhat adhesive and clots together, and at about 50° forms a soft mass, at the same time darkening in colour; when

this mass is cooled down, it is found to have the brittleness, and, if it has been pressed together, the fracture of the vitreous form. This clotting together on warming is a character of the powders of viscous liquids, as is illustrated by the following experiment:—Some sealing-wax was reduced to as fine a powder as possible in a mortar, then placed in water and warmed. The powder became first of all adhesive, and at 40° — 50° began to clot together. On further raising the temperature, it became quite soft, and after cooling down, it assumed the ordinary brittleness of sealing-wax. The behaviour of amorphous selenium is so exactly similar that it would scarcely have been possible to tell which of the two substances was in hand but for the difference in colour. By placing some of the powder in a pastille press, and striking a few sharp blows upon it with a hammer, a hard black mass is obtained, which has a conchoidal fracture, though less brilliant than that of vitreous selenium prepared in the ordinary way. The red powder is never quite free from dust, which interferes with the experiment. These properties all go to show the identity of the amorphous and vitreous forms. If there be any difference at all between them it is a very slight one, and would not justify their being considered as two distinct modifications. For a discussion of the possibility of such a difference, see the section on specific gravities. Hittorf (1848), Regnault (1851), and others, have remarked upon their identity. The amorphous form of selenium is the one which separates by preference in all cases where selenium is rapidly set free, either by decomposing one of its compounds or by precipitation from solution or vapour. This is in accordance with the rule laid down by Ostwald (*Zeit. Phys. Chem.*, 1897, xxii., 294). The amorphous form is obtained in any of the following ways:—

- (1). In the ordinary method of purification by dissolving in potassium cyanide and then re-precipitating with hydrochloric acid.
- (2). When selenious acid is reduced by sulphur dioxide. Even if both solutions be previously heated, it is still the amorphous form which comes out. In order to test this further, a boiling solution of selenious acid was added to a boiling solution of potassium sulphite; now at 100° vitreous or amorphous selenium goes over rapidly into the metallic modification; nevertheless, on mixing the above solutions, the selenium makes its appearance first as a red precipitate, and only after the lapse of a certain time does this become black. In place of sulphur dioxide we may use, in this reaction, iron, zinc, hydrogen, phosphorous acid, stannous chloride, ferrous chloride, chromous chloride, &c. Klages (1898) records that there is an emission of light when selenious acid is reduced by hydrogen.
- (3). From solutions of selenium in concentrated sulphuric acid, on the addition of water.
- (4). By the decomposition of selenious bromide by alcohol (Schneider, 1866).
- (5). By sublimation of the element itself, whereby the amorphous form condenses in the cooler parts of the tube, though it is possible also to obtain crystals of the grey form in this way (Borntäger, 1881).
- (6). From various compounds of selenium when decomposed, such as the alkaline selenides (Uelsmann, 1860).
- (7). By the electrolysis of solutions of selenious acid, or by passing a current through a selenium cell, whereby amorphous selenium makes its appearance at the anode (Bidwell).

When melted selenium is rapidly cooled, the vitreous form is always obtained. This case is not like the above, being merely an instance of supercooling.

Amorphous and vitreous selenium show an increased reactivity compared with the other forms. This is of importance in the purification of the element by the cyanide method, because if selenium be heated in a solution of potassium cyanide, it goes over to the metallic form, and long boiling is then required to bring it into solution;

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

whereas if the amorphous or powdered vitreous material be placed in a cold cyanide solution, the reaction is complete in a very short time. This fact was observed by Schjellerup (*Ann.*, 1859, cix., 125), but has been lost sight of in most of the more recent work. Its bearing upon analytical methods and upon commercial processes might prove important.

Behaviour of Amorphous Selenium in Solvents.

Mitscherlich (1855) observed that when amorphous selenium is allowed to stand in carbon disulphide for some weeks, it becomes darker in colour and more compact, and changes to a mass of red crystals which are, like the original substance, completely soluble in carbon disulphide, though not readily so. The observation was repeated by Schneider (1866), and later by others. Wishing to repeat the experiment and to find whether the change is influenced by light, I proceeded as follows:—

Experiment 44.—A small quantity of amorphous selenium was placed in carbon disulphide, the tube sealed and allowed to stand in diffused light. After one day the selenium had become very dark in colour, and showed bright crystal faces. On stirring the tube, it was found that this change was only superficial; but upon exposing fresh surfaces, these darkened very rapidly, and in two days the mass had become entirely crystalline in appearance, and had assumed a uniform deep cherry-red colour. The volume of the selenium had also materially diminished. This leads to the conclusion that the change into the crystalline modification goes on much faster than had been supposed, and also that it is in some way affected by light. How far the light effect goes will be better understood from the following experiment:—

Experiment 50.—Amorphous selenium in a tube of carbon disulphide, in the dark. After seven days the mass of selenium had become almost entirely crystalline, but showed no change of colour. After standing for twelve days longer, the colour was a dark cherry-red, much deeper than the original colour, and the entire mass had become crystalline. This change of colour between the two periods may have been due to the exposure of the tube on the first examination, or it may be that the crystals ultimately assume the deeper colour even in the dark. Detailed experiments to trace out the connection between these colour changes were not undertaken, but it is clear that the absence of light, though it retards the darkening of colour, does not prevent the formation of crystals. A later experiment in direct sunlight showed a complete change in one day, the mass becoming uniformly dark in colour and completely crystalline.

After these experiments, I turned to the consideration of the behaviour of amorphous selenium in contact with other liquids.

Experiment 53.—In water. After four days, there was no visible change; after eight days, a perceptible darkening; after fourteen days, this change of colour had become more distinct, but no crystal faces could be observed. During this period of time, the tube had stood at least three afternoons in direct sunlight. After one hundred days, the colour was much darkened, but still red.

Experiment 52.—In absolute alcohol. After four days the powder had become noticeably darker in colour, and this change progressed steadily to the end. After eleven days crystal faces made their appearance, and after fifty days the mass was everywhere crystalline and almost completely black.

Experiment 51.—In benzene. After three days there was a visible change of colour. After four days glittering crystal faces became noticeable, and after six days the mass had assumed a uniform deep maroon, or cherry-red colour, and was everywhere crystalline. During ten days more, there was no change in appearance, and the experiment was then stopped. Experiments 51 and 52 were made under the same conditions as 53 with regard to sunlight.

Experiment 56.—In quinoline. The material becomes black at once, in diffused daylight. Under the microscope the progress of the change may easily be watched. It spreads gradually through the mass under ordinary illumination, and is almost instantaneous in direct sunlight. There is no perceptible shrinking together of the selenium, hence the change is probably not the same as that which is brought about in amorphous selenium by raising the temperature. It remains here in a state of extremely fine division, and when shaken with the quinoline, does not settle again to the bottom for hours. After the first half hour no further change in colour could be observed, although the period of observation extended over forty days. It was impossible to find any signs of crystallinity either with the eye or under the microscope. At the close of the experiment, the selenium was removed from the tube, washed with benzene, and dried. It showed no sign of melting at 215°, but at 225° melted at once. When shaken in carbon disulphide, it remained for a long time suspended in the liquid—much longer than ordinary amorphous selenium—but, on filtering, the solvent came through clear and colourless.

This shows beyond a doubt that the material goes over in quinoline, to the metallic form, and not to the crystalline modification which is obtained, as we have seen, in other liquids. There is here not merely a difference in the rate of change, but a difference in its nature, brought about by the presence of the liquid. It was important then to learn a little more of this change.

A larger quantity of amorphous selenium was placed in quinoline, in diffused light. It remained unchanged for a few moments, then began to darken rapidly, and in fifteen minutes was completely black. After thirty minutes benzene was added, and the material filtered and dried. It did not melt at 200°. The specific gravity was found to be 4.65. A second determination after further washing and drying gave 4.59. The variation is somewhat large, but it must be remembered that only a small quantity of material was used. The results show at least that the change to the metallic form was not yet complete. A larger quantity—about 1 grm.—of amorphous selenium was then placed in quinoline, and left for two days. At the end of that time a specific gravity determination yielded the result 4.86. Hence the change, which is at first so rapid, is only superficial. It is probable that each little particle of the amorphous form becomes covered with a coating of the metallic modification which then protects it from further immediate change.

The question arises, whether the action of quinoline is catalytic, or whether it is an effect of solubility, or in some other way proportional to the amount of that liquid present. To answer this, five experiments were made in liquids composed of benzene and quinoline in the following proportions:—

- | | | |
|------|--------------|---------------------|
| (1). | Pure benzene | |
| (2). | 2 c.c. " | +0.1 c.c. quinoline |
| (3). | 2 " " | +0.2 " " |
| (4). | 2 " " | +0.5 " " |
| (5). | 2 " " | +2.0 " " |

The selenium in No. 5 blackened within a couple of minutes. That in No. 4 was perceptibly slower in changing, but reached the same end state. In No. 3 it was still not entirely blackened after twenty minutes, and that in No. 2 was, after twenty minutes, only very slightly darker than that in No. 1, which had shown no change at all. On the following day, all except No. 1 were completely black. In (4) and (5) the substance remained, after shaking, a long time in suspension. In the others this was much less marked. It appears from these experiments that the velocity of the change is roughly proportional to the concentration of the quinoline.

An experiment to find whether the reaction goes on in the absence of light showed that it did so, although the results were not accurate enough to show whether the velocity suffers a diminution in the dark.

(To be continued).

NOTICES OF BOOKS.

Chemical Technology, or Chemistry in its Applications to Arts and Manufactures. Edited by C. E. GROVES, F.R.S., and W. THORP, B.Sc. With which is incorporated Richardson and Watts's "Chemical Technology." Vol. III. *Gas Lighting.* By CHARLES HUNT. London: J. and A. Churchill. 1909. Pp. 312.

GAS LIGHTING in this country is not yet a century old, and although the electric light is now a powerful rival, inasmuch as it is cleaner, more convenient, and safer than gas, the introduction of the Welsbach and other incandescent burners will no doubt enable it to maintain its important place as an illuminating agent.

The first Gas Company obtained its Act of Incorporation in the year 1810, two years later it was granted a Charter, and was then known for nearly sixty years as the Chartered Gas Company. In 1850 there were thirteen Companies in London; the inconvenience of this was found to be so great that they were eventually induced to amalgamate and form the three which now supply the whole of the metropolitan area from nineteen different gas works.

The process of gas-making is made clear in Chapter II., which is furnished with the plan and section of a modern gas-plant illustrating the complete description given; numerous analyses of gas coal are quoted in the following chapter. This is followed by details of the process of manufacture and the machinery necessary for the operations.

The various methods for the removal of tar and other by-products are next discussed, together with the necessary washers, scrubbers, purifiers, &c.

Chapter XII. treats of the ammoniacal liquor; full details of an analytical method for determining its value are given, and also descriptions of the more important apparatus devised either for obtaining "*liquor ammoniac*" from it, or for converting it into sulphate of ammonia.

Another important class of subsidiary products of gas-making are the cyanogen compounds; these are also fully dealt with.

The storage of gas and its distribution are next considered and the various kinds of gasholders described; after which we have a chapter on gas-meters, both wet and dry. The wet meter had many disadvantages, and has now been almost entirely superseded by the dry one.

Then follows a chapter on processes for enriching ordinary gas by the use of volatile hydrocarbons, and the Dinsmore process for enrichment by means of coal-tar is also fully described.

The last section of this work is on gas-burners, many different kinds of which are fully described. In conclusion, we have a full account of incandescent gas-burners; these have already effected a revolution in gas-lighting from the brilliancy of the light and the economy arising from the relatively small amount of gas they consume.

The book is profusely illustrated, and is a valuable addition to the literature of the subject.

Action of Light on Solutions of Ferrocyanide of Potassium treated with Peroxide of Hydrogen.—V. A. Kistrakovsky.—A solution of ferrocyanide of potassium exposed to direct sunlight, acquires an alkaline reaction which gradually disappears in darkness owing to the absorption of CO₂. If we pass a current of air through the ferrocyanide solution in faint diffused light the alkaline reaction is not produced; the voltaic arc causes it to appear slightly. The addition of peroxide of hydrogen greatly increases the sensitiveness. The alkaline solution of ferricyanide is decolourised where exposed to the light. The author has examined the occurrence of these phenomena, and will shortly publish further experiments.—*Journ. Soc. Phys. Chim. R.*, vol. xxxi., p. 669.

CORRESPONDENCE.

THE

BASES CONTAINED IN SCOTTISH SHALE OIL.

To the Editor of the Chemical News.

SIR,—In a paper on the above subject, read before the Chemical Society on November 15th, Messrs. Garrett and Smythe say:—"But little attention has been paid to those present in shale oil." From this I conclude that they are not acquainted with the work which Mr. G. Carr Robinson and Mr. W. L. Godwin have done in elucidating the composition of the basic shale tars. Their papers will be found in the *Transactions of the Royal Society of Edinburgh*, vols. xxviii. and xxix.

It will be interesting, however, to see whether Messrs. Garrett and Smythe succeed in nitrating these bases, and thus making them available for the manufacture of colouring matters. At present they are burnt under the stills as fuel—I am, &c.,

WM. B. SYME, F.I.C.

Addiewell, December 8, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 21, November 19, 1900.

Direct Combination of Nitrogen with the Metals of the Rare Earth Group.—Camille Matignon.—M. Maquenne described a method (*Comptes Rendus*, cxxi., p. 1147) in which the direct union between nitrogen and the alkaline earth metals was effected. The author utilises the above method to study qualitatively, in a systematic manner, the action of certain gaseous bodies on those metals which are difficult to procure in the free state or those which have not as yet been isolated. He finds that this method of operation is general and convenient for the qualitative examination of the direct action of certain gaseous or solid bodies on the rare earths. Nitrogen unites directly and rapidly on the following metals:—Thorium, cerium, lanthanum, praseodymium, neodymium, and samarium. Argon does not combine rapidly with the same metals at the temperature of the experiment. Magnesium reduces the oxides of praseodymium, neodymium, and samarium; it being known already, from Winkler's experiments, that this reduction liberates thorium, cerium, and lanthanum from their oxides. The heat of formation of thorium and cerium oxides is higher than that of the other oxides; samarium oxide is apparently the least exothermic. A slight modification of the above method allows of the isolation of the above metals mixed with magnesium. The author is continuing this research in the hope of obtaining the above metals, their nitrides, and their hydrides in a state of purity.

Relation between the Chemical Constitution of the Colouring-matters derived from Triphenylmethane, and the Absorption-spectra of their Aqueous Solutions.—P. Lemoult.—The author experiments on the spectra of various artificial colouring-matters. He comes to the conclusion that the colouring-matters derived from triphenylmethane, which contain, as is generally the case, at least two atoms of nitrogen triply combined to the central carbon, give, when in aqueous solution, an absorption-spectrum containing a band in the luminous red portion of the spectrum when a grm.-molecule is in solution in 1000 litres of water and a thickness of 6 m.m. is used;

the middle of this band occupies an invariable position (wave-length about 6860) for those colouring-matters which have not more than two atoms of tertiary nitrogen, and an invariable but different position (wave-length about 6660) for those which have a third tertiary nitrogen.

Chlorophylline Blue.—M. Tavett.—In chlorophyll, when defined as the whole of the pigments producing the green colouration of plants, certain yellows and greens have been described. These the author divides into two groups, which may be called the xanthophylline group and the chlorophylline group. The xanthophylline group (carotene, erythrophyll, chrysophyll, &c.) only absorb rays of short period and are not luminescent. The chlorophyllines are fluorescent, and possess, among other things, a characteristic absorption in the red portion of the spectrum. The present paper contains an account of researches made on one of these latter—chlorophylline blue. This substance can be prepared by heating the plant with fine sand, and adding eventually magnesia or calcium carbonate to neutralise the cellular juice. The colouring matter is taken out by benzene, and after undergoing various operations to separate it from the other colouring-matters, an alcoholic solution of the blue pigment is formed. This is slowly evaporated in the cold and crystallises out in minute crystals of an inky black appearance.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 12.

The Action of Iodides and Hydriodic Acid on Sulphurous Acid.—A. Berg.—Already inserted in full.

On two Polysulphides of Lead and Copper.—F. Bodroux.—Already noticed.

On a Chlorosulphide of Mercury.—F. Bodroux.—Already noticed.

Crystallised Selenide of Manganese and an Oxy-selenide.—M. Fonze-Diacon.—Already inserted in full.

An Arsenide of Nickel.—Albert Granger and Gaston Didier.—Already noticed.

Action of Ethylic Mercaptan on some Diatomic Acetones.—B. Laguet.—Ethylic mercaptan reacts on benzoin in the presence of the dehydrating agents hydrochloric acid or chloride of zinc. It suffices to pass a current of dry hydrochloric acid gas through a mixture of benzoin and mercaptan in excess, or to add finely powdered fused chloride of zinc to the mixture. The transformation into mercaptol is complete in both cases. The solid product obtained is treated and crystallised several times in dilute alcohol; it then appears in the form of white needles fusing at 93–94° without decomposition. Ethylic mercaptan also reacts in a similar manner on benzile, giving white prismatic needles when crystallised in alcohol, and octahedra in acetic acid, both fusing without decomposition at 73–74°, and on acetylacetone, giving a liquid product which decomposes on distillation even under reduced pressure; it has the appearance of an amber-coloured oil, is insoluble in water and has a strong disagreeable odour; its density at 13.5° is 2.008.

Ethyloxalic Anhydride.—L. Bouveault.—Ethyloxalic anhydride is a colourless liquid of a consistency like glycerin, boiling at 135° under 10 c.m. pressure. Its composition is found on analysis to be $C=44.30$, $H=4.88$; calculated for $C_8H_{10}O_7$, $C=44.04$, $H=4.59$. It absorbs water with avidity, giving crystals of oxalic acid.

Synthesis of α -Methyl- β -benzoylpropionic (Phenylmethylbutanonic) Acid.—T. Klobb.—Twenty grms. of pyrotartaric anhydride, 40 grms. of $AlCl_3$, and 250 grms. of benzene are heated on the water-bath in a flask fitted with a vertical condenser, for an hour and a half to two hours. The contents of the flask are then treated, while still warm, with water containing a little hydrochloric acid. When the reaction is finished, the upper, almost

colourless, benzenic layer, is separated, filtered, and left to crystallise. The acid, $C_{11}H_{14}O_3$, is deposited in white needles; these are purified by crystallisation in boiling water. The acid, though soluble at 100°, is almost insoluble in cold water. Phenylmethylbutanonic acid melts at 135–136°.

The Acetals of the Phenols.—R. Fosse.—Already noticed.

Action of Chloride of Ethylidene on the Cresols and on Resorcin.—R. Fosse and J. Ettlinger.—Already noticed.

Action of Isocyanate of Phenyl and of Aniline on some γ -Ketonic Acids (II.).—T. Klobb.—Already noticed.

The Compounds of Basic with Acid Colouring Materials.—A. Seyewetz.—Already noticed.

Action of Fuming Nitric Acid on Camphene.—L. Bouveault.—According to accepted ideas, the product of the fixation of the molecule of nitric acid on camphene

should be represented by $C_8H_{14} \begin{matrix} \text{CH-O-NO}_2 \\ | \\ \text{CH}_2 \end{matrix}$, which

makes a nitric ether of a secondary alcohol. It has been shown that the nitric ethers of the secondary alcohols, saponified by potash, give nitrite of potassium and an acetone. In applying this rule to nitrate of camphene, an abundant crystalline precipitate of nitrate of potassium was formed without a trace of nitrite, and the alcoholic solution contained camphene almost exclusively.

On Santalenes and Santalols.—M. Guerbet.—Already noticed.

The presence of Dextrose and Levulose in the Leaves of Beetroots.—L. Lindet.—The author gives several tables of results of the analysis of the sap or juice of the leaves. Samples taken on July 3rd contained 0.89 grm. of dextrose and 0.13 grm. levulose per 100 c.c. of juice; by the 20th, the quantity of dextrose had increased to 2.80 grms. and then decreased again to 1.24 grms. by October 8th. The levulose increased to 0.53 grm. on July 12th, and, after varying between that figure and 0.11 grm., it finally reached 0.37 grm. on October 8th. The proportion of levulose per cent of dextrose varied from 6 to 35.

Essences of Lavender and the Causes of the Variation in their Contents in Ether.—MM. Jeancard and Satie.—Altitude appears to play a secondary part in the proportion of ether present in essences of lavender. The method of distillation is an important point in the richness of the essence in ether. The distillation should not be pushed too far, and should be done as rapidly as possible. The quality of the water used also has an influence; the water should only leave a small residue when evaporated to dryness.

Colorimetric Estimation of Vanadium.—L. Maillard.—Already inserted in full.

Estimation of Lead by Electrolysis in the Sulphate and Chlorides. Application to the Analysis of Lead Glass and Chromates of Lead.—Ch. Marie.—Already inserted in full.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The Managers reported that at their Meeting held that day they had elected Dr. Allan Macfadyen Fullerton Professor of Physiology for three years (the appointment dating from January 14, 1901). The following were elected members: Mr. J. Augier, Mr. E. Barclay, Mr. R. T. Baylis, Mr. H. P. Boulpois, Mrs. E. Hills, and Mr. R. Taylor.

Ruthenium and its Compounds. Chlororuthenate of Potassium (II).—V. Antony and A. Lucchesi.—Chlororuthenate of potassium, RuCl_6K_2 , is obtained by melting together, in a silver crucible, a quantity of ruthenium with 6 parts of KOH, and then adding enough chlorate of potassium to the melted mass to dissolve the whole of the metal. It is further heated to destroy the whole of the chlorate. The mass, which is green when hot and orange-coloured when cold, dissolves in water which has been slightly acidulated with hydrochloric acid, and gives a dark red solution. When evaporated, cold, in vacuo over CaO, it deposits the chlororuthenate in the form of a micro-crystalline red powder, scarcely soluble in water and quite insoluble in the presence of potassic chloride. It is decomposed by hot water. This salt has been analysed by decomposing it, at a dull red heat, in a current of hydrogen; the loss of chlorine was first determined, and then the potassic chloride by lixiviation. Finally, there remained nothing but ruthenium.—*Gazz. Chim. Ital.*, (2), xxix., p. 82.

Estimation of Chromium in Iron and Steel.—E. Dohler.—From 2.5 to 5.0 grms. of the substance are weighed out and dissolved in a matras of 750 c.c. capacity, with 30 c.c. of hydrochloric acid of 1.19 density, and 100 c.c. of water. After complete solution about 750 c.c. of cold water are added, and then an excess of a milk of carbonate of barium. This is left to stand for about twelve hours, keeping the air from it as much as possible by covering the vessel with a watch glass. Most books on chemistry state that this precipitate will contain the whole of the chromium and the aluminium, as well as small quantities of iron. This, however, is not the case, for the filtrate submitted to fresh treatment with carbonate of barium will, on each successive occasion, give up unmistakable quantities of chromium and a good deal of ferric oxide. It is therefore necessary to precipitate at least twice. The two precipitates are dried, and separated from the filter as much as possible; the filters are incinerated in the same porcelain crucible in which the precipitates are placed, and the whole melted with a mixture composed of 5 grms. of anhydrous sodio-potassic carbonate and 2 grms. of saltpetre. The alkaline chloride formed is taken up with warm water, filtered to remove the iron and the excess of carbonate of barium, and evaporated in the presence of hydrochloric acid to separate the silica; in the filtrate the chromium is separated from the aluminium, and weighed in the state of oxide, Cr_2O_3 .—*Chem. Zeitung*, xxiii., p. 868.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Pure Zinc.—I should be greatly obliged if any of your readers could tell me of any special purpose, other than German silver or Leclanché rods, for which especially pure zinc (99.90 per cent) would be valuable.—AL. X. E. TUCKER.

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8. (Cantor Lectures). "Electric Oscillations and Electric Waves," by Prof. John A. Fleming, M.A., D.Sc., F.R.S.

WEDNESDAY, 19th.—Society of Arts, 8. "The Siege of Ladysmith," by W. T. Maud (Special Artist to the Graphic). Microscopical, 8. Demonstration of Lantern Projection in conjunction with the Microscope, by Mr. Barton.

THURSDAY, 20th.—Chemical, 8. "On the Union of Hydrogen and Chlorine," by J. W. Mellor, B.Sc.

ERRATUM.—P. 271, col. 2, line 4 from bottom, for "voltmeter" read "voltmeter."

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VOL. LXXXII., No. 2143.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART VI.

By HARRY BREARLEY.

(Continued from p. 282).

SULPHUR (continued).

Sulphur in Fuels.

803. STORER (C. N., xxi., 196).—Coal, pyrites, or free S may be oxidised by heating with $\text{HNO}_3 + \text{KClO}_3$. The BaSO_4 is precipitated from tartaric solutions, and washed with $\text{Am}\bar{\text{A}}$ to remove adherent $\text{Ba(NO}_3)_2$.
804. BRADBURY (C. N., xxxviii., 147).—Part of the sulphur in coal, *i. e.*, that organically combined, is not oxidised to H_2SO_4 by treatment with acids.
805. DROWN (C. N., xliii., 89).—By separate treatment with NaHO , Br , and HCl , S existing as pyrites or soluble sulphate is dissolved; that organically combined, not. For total S, burn in O, absorb gases in KMnO_4 , and fuse the residue.
806. WALLACE (C. N., xli., 201).—Sulphur must exist organically combined when no sulphates are present and not nearly enough iron to form the bisulphide.
807. HELM (J. I. S. I., 1882, 345).—Gaseous and liquid S compounds are evolved from coal at a temperature below the decomposition of FeS_2 or the volatilisation of S, and therefore part of the sulphur is organically combined.
808. MUCK (J. I. S. I., 1886, 866).—Evidence that S in coal may be organically combined. The coal containing least sulphur does not necessarily produce the purest coke.
809. BLUM (C. N., lviii., 65).—Wet oxidations remove only such S as is combined with Fe or Ca. Total S obtained by fusion with $\text{KNO}_3 + \text{NaCl} + \text{Na}_2\text{CO}_3$.
810. GRITNER (J. C. S., lxiv., ii., 89).—Estimates S in coal ash by treating with Br and HCl , precipitating Fe with AmHO , and adding BaCl_2 . This amount subtracted from "total" gives "combustible S."
811. CALVERT (C. N., xxiv., 76).— CaSO_4 should be distinguished from FeS_2 in coal analysis. Boil with H_2O , estimate CaSO_4 in filtrate, oxidise residue with aqua regia, and fuse dried mass with Na_2CO_3 . HNO_3 prevents precipitation of BaSO_4 . In the direct oxidation with aqua regia, sub-sulphate of iron becomes firmly attached to the carbonaceous mass.
812. REICHERT (C. N., xxi., 35).—Ignite charcoal with KNO_3 ; estimate S as usual.
813. A. A. (C. N., xxiii., 30).—Add powdered coke to fused KClO_3 or KNO_3 , and precipitate acidified solution with BaCl_2 .
814. NAKAMURA (C. N., xl., 237).—Heat with mixed alkaline carbonates over a spirit-lamp. Precipitates as usual.
815. ASBOTH (J. C. S., lxx., ii., 448) and GLASER (J. C. S., lxxiv., ii., 483).—Fuse with Na_2CO_3 and Na_2O_2 , boil acidified solution with Br , and precipitate as BaSO_4 .
816. ATKINSON (J. S. C. I., 1886, 154).—As in 780. By heating pyrites with Na_2CO_3 , not more than 96 per cent of the S is retained (see 860).

817. STOLBA (J. S. C. I., 1888, 524).—Mix with equal amounts of Ag powder and KHCO_3 , heat residue with AmNO_3 , and precipitate as usual.
818. STOCK (C. N., xxx., 211).—Mix coal to paste with CaO , ignite, add AmNO_3 ; re-ignite, dissolve in HCl , and add BaCl_2 . Koninck and Nihoul (J. C. S., lxxviii., ii., 136) use $\text{CaO} + \text{Ca(NO}_3)_2$.
819. ESCHKA (C. N., xxxi., 261).—Heat powdered fuel with $\text{Na}_2\text{CO}_3 + \text{MgO}$, re-heat with AmNO_3 , leach, and precipitate S.
820. ROTHE (J. S. C. I., 1891, 952).—The roasting of 819 may be done in porcelain crucibles with less danger of S contamination from the gas.
821. HUNDESHAGEN (C. N., lxvi., 169; and lxxviii., 49).—By using $\text{K}_2\text{CO}_3 + \text{MgO}$ instead of Eschka mixture (819) the combustion is more rapid and the loss as H_2S obviated; this applies to fuels rich in volatile S.
822. HANDY and CAMP (C. N., lxvii., 90).—Hundeshagen's modification is no improvement on the original.
823. PATTINSON (C. N., xxxix., 30).—As 818, omitting AmNO_3 treatment. Determines total S and S in ash.
824. ANTONY and LUCCHESI (J. I. S. I., 1899, ii., 492).—Heat with $\text{MnO}_2 + \text{KMnO}_4 + \text{Na}_2\text{CO}_3$, acidulate with HNO_3 , and precipitate as BaSO_4 . As accurate as 819, and quicker.
825. PRUNIER (J. C. S., lviii., 290).—Heat with KMnO_4 , pass gases into KMnO_4 , digest residue with water, add to absorbing KMnO_4 , and treat with HCl and BaCl_2 .
826. NEILSON (C. N., lxiii., 192).—Fuse coke with Na_2CO_3 and MnCO_3 , evaporate with HCl , and precipitate as BaSO_4 . Compares with CaO , MgO , and alkaline fusion processes.
827. MIXTER (C. N., xxvii., 53; and xlvi., 217).—Burn substances in O and condense H_2SO_4 from the gaseous products. Elaborate apparatus, but process widely applicable. A description of Sauer's process.
828. SAUER (C. N., xxviii., 226).—Burn in O, absorb SO_2 in bromised HCl . See also Marchlewski (J. C. S., lxiv., ii., 551).
829. BERTHELOT (J. C. S., lviii., 1462).—Burn with O at 25 atmospheres in a calorimetric bomb; the S is converted to H_2SO_4 .
830. HEMPEL (J. C. S., lxiv., ii., 187).—Burn the coal electrolytically in a glass bottle, complete oxidation with Br , and precipitate with BaCl_2 .
831. BRUHLE (J. S. C. I., 1889, 219).—Heat mixture of coal and oxidant in a covered boat, to prevent escape of SO_2 . Results higher than by open fusion.
832. BAILEY (J. S. C. I., 1889, 360).—Imperfections of various methods; prefers 819.

Sulphur in Pyrites, &c.

833. YARDLEY (C. N., xxv., 257).—Pyrites oxidised at high temperatures with HNO_3 do not loose H_2SO_4 , but low temperatures are more favourable both to the decomposition of the ore and the precipitation of the BaSO_4 .
834. LUNGE and BRODENRIG (C. N., lxviii., 285; and lxi., 76).—In opening pyrites with aqua regia, HNO_3 not stronger than 1.42 should be used. Oxidise with Br and HNO_3 , and separate Fe by pouring into AmHO ; the excess must not be boiled off or basic ferric sulphates form.
835. WÖHLER (C. N., xviii., 72).—Pyrites suspended in water is completely dissolved on passing hypochloric acid.
836. JOHNSON (C. N., lxx., 212).—Decompose pyrites with HNO_3 and KClO_3 , reduce Fe in HCl solution with hypophosphite (which also destroys traces of HNO_3), and precipitate with BaCl_2 .
837. STANSBIE (C. N., lxxiv., 189).—Oxidise the sulphide (or even pure S) with HNO_3 and Br . Or heat with CaO ; precipitate S as usual.

838. WESTMORELAND (*J. S. C. I.*, 1887, 84).—Lunge's old and new methods give like results. Only small excess of BaCl_2 should be used and HCl used sparingly in the washing.
839. LUNGE (*J. S. C. I.*, 1887, 95).—Galena does not materially interfere when pyrites is opened up with aqua regia.
840. NOAILLON (*J. C. S.*, lxxii., ii., 595).—Oxidise mineral sulphides with $\text{HNO}_3 + \text{NaClO}_3$, evaporate with HCl , and finish as in 834.
841. TESCHEMACHER and SMITH (*C. N.*, xxiv., 61, &c.).—Precipitated BaSO_4 carries down K , Ba , Cu , Mg , Fe , &c.; it is noticeably soluble in dilute HCl and HNO_3 , and ignited over gas is considerably reduced. Decompose pyrites and titrate HCl solution as in 857.
842. GLENDINNING and EDGAR (*C. N.*, xxiv., 140; and xxvii., 13).—Solubility of BaSO_4 in HCl exaggerated in 841. Gravimetric estimation of S in pyrites a reliable process. Great discrepancies may arise from grinding the mineral in wedgwood or porcelain mortars.
843. GLADDING (*C. N.*, lxx., 181).—Nitrates cause high results; chlorides cause no error. Results low through Fe being precipitated as ferric sulphate. When Fe is precipitated with Am , a little S remains with the $\text{Fe}_2(\text{HO})_6$. Oxidise pyrites with HNO_3 and Br . BaSO_4 is insoluble in Fe_2Cl_6 .
844. LUNGE (*C. N.*, lxxi., 132).—There is no advantage in 843 so far as it professes to be a modification of 834. BaSO_4 is distinctly soluble in acid Fe_2Cl_6 . Process 836 is unworkable.
845. GLADDING (*J. C. S.*, lxx., ii., 622 and 672).—If BaCl_2 be not added in drops it contaminates the BaSO_4 . Lunge contends that it makes no practical difference how the BaCl_2 is added.
846. KÜSTER and THIEL (*J. C. S.*, lxxvi., ii., 247 and 805).—Prevent Fe contaminating BaSO_4 by adding oxalate or tartrate (see 795); or precipitate Fe with AmHO , add BaCl_2 , and then re-dissolve the $\text{Fe}_2(\text{HO})_6$ with HCl .
847. MACAGNO (*C. N.*, xliii., 192).—Digest S ore with a known amount of CS_2 , determine its specific gravity, and read off the amount of S dissolved from tabulated observations.
848. SMITH (*C. N.*, lxii., 206).—Sulphides are oxidised to H_2SO_4 by mixing with molten KHO and passing electric current. BaSO_4 precipitated in a solution free from Fe , &c.
849. REICHARDT (*C. N.*, xlii., 259).—Iron and copper pyrites are oxidised with Br water.
850. LUNGE (*C. N.*, xl., 184).—Dry processes attack both galena and heavy spar, and this partly accounts for the results being higher than by the wet processes.
851. GLASER (*C. N.*, lxx., 179), CLARK (*J. C. S.*, lxiii., 1080), and ASBOTH (*J. C. S.*, lxx., ii., 71).—Fuse with Na_2O_2 , add HBr , acidify, boil off Br , and add BaCl_2 .
852. DEUTECOM (*C. N.*, xlii., 317) and BOCKMANN (*C. N.*, xlv., 95).—Decompose with $\text{Na}_2\text{CO}_3 + \text{KClO}_3 + \text{NaCl}$; precipitate as usual.
853. CLARK (*J. S. C. I.*, 1885, 329, 573, and 724).—Heat powdered pyrites with $\text{MgO} + \text{NaHO}$, precipitate Pb with CO_2 , acidify, and add BaCl_2 .
854. KELLER and MAAS (*J. C. S.*, lxx., ii., 498).—Copper pyrites and roasted ores are opened up with KHO and Na_2O_2 .
855. JANNASCH (*C. N.*, lxi., 114 and 124).—Heat in bromised air and absorb gases in HCl and tartaric acid. Br may be replaced by HNO_3 . Later, simple ignition in oxygen is preferred (see 827).
856. HINDS (*C. N.*, lxiii., 285).—Measure the height of a column of liquid containing the BaSO_4 through which a candle flame is just visible. The percentage $\text{H}_2\text{SO}_4 \times \text{depth of column}$ is a constant. AGLOT (*J. C. S.*, lxxii., ii., 431).—Accurate results can be obtained only in alcoholic solutions.
- I. b. Volumetric Estimation.*—
857. WRIGHT (*C. N.*, xvii., 122).—Oxidise pyritic ore with aqua regia, add small excess BaCl_2 , and then Na_2SO_4 until neither Ba nor SO_3 is in solution. Other methods of oxidising the ore; one suitable in case Pb is present.
858. HOLLAND (*C. N.*, xxvii., 15).—A point is reached in 857 when either H_2SO_4 or BaCl_2 will produce a precipitate in the filtered liquid. Pyrites decomposed by fusion in a closed tube carrying a delivery tube.
859. BERINGER (*C. N.*, lix., 41).—The titration of H_2SO_4 with BaCl_2 is best made in an acetic solution containing soda acetate. A true finishing-point is arrived at (858). The interference of many metals observed.
860. PELOUZE (*C. N.*, v., 45).—Heat powdered pyrites with $\text{Na}_2\text{CO}_3 + \text{KClO}_3 + \text{NaCl}$. The Na_2CO_3 which has not combined (see 816) with the sulphur is titrated. Neither Si , Ba , nor Ca interfere.
861. WATSON (*J. S. C. I.*, 1888, 305).—Heat burnt pyrites with Na_2CO_3 alone, and titrate as in 860. Soluble sulphur is determined by boiling with standard Na_2CO_3 .
862. LUNGE (*J. S. C. I.*, 1893, 292).—Heat as in 861, short of fusion, and extract with NaCl . H_2S may be evolved from FeS when treated with nitrohydrochloric acid; oxidise with HNO_3 and then add HCl (see 771).
863. SCHWARZ (*C. N.*, viii., 207).—Add PbNO_3 , filter off PbSO_4 , and titrate excess Pb with $\text{K}_2\text{Cr}_2\text{O}_7$, using AgNO_3 indicator. Pellet (*C. N.*, xxxiii., 9) used same process, but estimates $\text{K}_2\text{Cr}_2\text{O}_7$ with FeSO_4 and KMnO_4 .
864. CLEMM (*C. N.*, xix., 287), GAWALOWSKI (*C. N.*, lviii., 72), and many others.—To neutral solution add BaCl_2 , then Na_2CO_3 to precipitate excess Ba , and titrate the residue of Na_2CO_3 with H_2SO_4 . NORTH (*C. N.*, lix., 58).—This process is worthless.
865. JEAN (*C. N.*, xxxiv., 272), HAUBST (*C. N.*, xxxv., 27), GROSSMAN (*C. N.*, xli., 114), and CHERIX (*J. C. S.*, lxiv., ii., 89).—Add $\text{Ba}(\text{HO})_2$, precipitate excess with CO_2 , and titrate the alkali (which was combined with the SO_3) with standard acid. Ca and Mg do not interfere.
866. FARNSTEINER (*C. N.*, lxvi., 296).—Add BaCl_2 precipitate excess in faintly ammoniacal solution with K_2CrO_4 , and titrate residual K_2CrO_4 with iodine. Similar processes, varying chiefly in the means of estimating the final K_2CrO_4 , are given by Precht (*C. N.*, xli., 24), Windish (*J. C. S.*, lxviii., ii., 137), and Marboutin (*C. N.*, lxxvi., 232), and others. Marboutin gives a resumé of volumetric processes for estimating S .
867. QUANTIN (*C. N.*, liv., 233).—Add excess of an HCl solution of BaCrO_4 ; SO_3 replaces CrO_3 ; precipitate excess BaCrO_4 with AmHO , and titrate the CrO_3 equivalent to the SO_3 with FeSO_4 . Processes on the same principle are given by Stolle (*J. C. S.*, lxiv., ii., 188), Reuter (*J. C. S.*, lxxvi., ii., 53), Baumann (*J. C. S.*, lxii., 104), and Andrews (*J. S. C. I.*, 1890, 328).
868. ASBOTH (*C. N.*, lxvi., 168).—The HCl solution of BaCrO_4 (867) is gradually decomposed, and is reliable only when freshly made.
869. SOLTSEIN (*J. C. S.*, lx., 115).—Add BaCl_2 , and titrate excess with $\text{K}_2\text{Cr}_2\text{O}_7$, using hæmatoxylin or logwood as indicator.
870. FREUND (*J. C. S.*, lxii., 1377).—Add excess BaHPO_4 , remove BaSO_4 , precipitate $\text{Ba}_3(\text{PO}_4)_2$ with Na_2CO_3 , dissolve precipitate in HCl , add Na_2SO_4 , and titrate H_3PO_4 in the filtered liquid on the principle that, to methyl-orange the acid is mono- and to phenolphthalein it is bibasic.
871. MARCHLEWSKI (*J. S. C. I.*, 1893, 375; and 1894, 283).—Comparative tests and criticism of various

oxidation and evolution methods. Andrew's process (867) can be used in the presence of Mg, Ca, Al, Zn, Fe, Ni, Co, and Ag.

872. COLSON (*C. N.*, xl., 205) and BURTON (*J. S. C. I.*, 1890, 330).—Burn in oxygen, and titrate SO_2 which has been collected in NaHO .

873. NABERY (*J. I. S. I.*, 1896, ii., 456).—As in 872 for coals; titrate excess NaHO with H_2SO_4 . Very little S remains with the ash.

(To be continued).

NOTE ON THE MARSH TEST FOR ARSENIC.

By CHARLES ESTCOURT, F.I.C., F.C.S.,
Public Analyst to the City of Manchester.

SULPHURETTED hydrogen is generated from the purest (arsenic free) granulated zinc obtainable, even when pure diluted hydrochloric acid is used.

Sulphuretted hydrogen is produced in nearly all experiments where sulphuric acid (even diluted) is used with the pure zinc.

Excess of sulphuretted appears to prevent the formation of the brown stain on the heated tube, even where good trace of arsenic is present. Thus, when sulphites are present in beer, scarcely any of the arsenic is obtained.

I use acetate of lead paper in the part of chloride of calcium tube nearest generating flask.

The whole matter deserves further investigation, as these reactions may account for many differences of opinion regarding presence of arsenic.

City Laboratory,
St. Andrew's Chambers, 20, Albert Square,
Manchester, December 14, 1900.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1900.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, December 10th, 1900.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during November has been below the average, though rain fell on twenty days out of the thirty; the actual rainfall was 1.65 inches, the average for the month is 2.42 inches, making a deficiency of 0.77

inch. This brings the total deficit for the year up to 3.22 inches, or 13.6 per cent on the thirty years' average.

Our bacteriological examinations of 541 samples have given the results recorded in the following table; we have also examined 39 other samples, from special standpipes, &c., making a total of 580 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	179
New River, filtered (mean of 128 samples) ..	5
Thames, unfiltered (mean of 26 samples) ..	1173
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 292 samples) ..	17
Ditto ditto highest	236
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	262
River Lea, from the East London Company's clear-water wells (mean of 43 samples) ..	5

Of the 463 samples of the filtered water supplied to London, examined bacteriologically during the past month, thirteen samples, or 2.8 per cent of the whole number of samples examined, contained more than 100 microbes per c.c. The water supply of the Metropolis continues to maintain the same high standard of purity as we recorded last month.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF SILVER.*

By LAUNCELOT W. ANDREWS.

(Concluded from page 287).

Experiments on the Influence of Dilution and Degree of Acidity.

IN the first series of experiments recorded below, a solution (slightly acid) of silver nitrate containing 0.7887 grm. of silver was used, and an empirical solution of starch iodide, of which 1 c.c. = 1.639 m.grm. of silver designated as "Sol. B."

From these results the following conclusions may be drawn:—

I. Within certain limits the amount of free nitric acid is without appreciable influence.

II. A considerable excess of iron solution is without influence.

III. For increasing dilution a very small correction is called for, which amounts to 0.10 m.grm. of silver for each 100 c.c. of solution. This correction is to be subtracted from the results directly obtained.

IV. If the solution titrated contains much more than 20 m.grms. of silver per 100 c.c. the results are too low in consequence of precipitation of silver sulphate with the iodide. This influence also appears in experiments numbered 58, 59, 62.

The object of the second series, experiments 56 to 62 inclusive, was to show the influence of lead salts upon the titration. It is apparent that there is no influence except when—in consequence of insufficient dilution—the precipitate of lead sulphate carries down silver sulphate with it, as is shown in numbers 58 and 62, and to a less extent in number 59, where the addition of 25 c.c. of water renders the results almost normal. That these errors are really due to the sulphate, and not to the lead, is shown by number 61, in which the same amount of

* Presented at the New York Meeting of the American Association for the Advancement of Science, June 28, 1900. From the *American Chemical Journal*, vol. xxiv., No. 3.

SERIES I.

Experiment No.	Ag solution. C.c.	H ₂ O added. C.c.	Dilute HNO ₃ added. C.c.	Nitrous acid or iron solution. C.c.	Iodide of starch required. C.c.	Remarks.
46	25	None	—	4 Sol. D	13'90	End reaction sharp.
47	25	250	—	20 Sol. D	13'25	" " "
48	25	None	1	2 Fe Sol. C	11'85	Ag ₂ SO ₄ precipitated.
49	25	None	5	2 "	11'85	" "
50	25	250	5	2 "	12'20	" "
51	25	250	5	2 "	12'17	" "
52	25	1000	5	2 "	12'65	" "
53	25	1000	20	2 "	12'67	" "
54	25	1000	20	8 "	12'63	" "
55	25	100	5	2 "	12'11	" "

SERIES II.—Two c.c. of Iron Solution (C) added in each Experiment.

Expt. No.	Ag solution. C.c.	H ₂ O added. C.c.	Dilute HNO ₃ added. C.c.	Pb or Cu solution. C.c.	Iodide of starch required. C.c.	Remarks.
56	25	250	5	10 N/10 Pb(NO ₃) ₂	12'21	
57	25	250	5	10 "	12'18	
58	25	None	5	10 "	11'57	Ag ₂ SO ₄ precipitated with PbSO ₄ .
59	25	25	5	10 "	11'97	" " "
60	25	250	5	10 "	12'20	
61	25	None	5	10 "	12'02	Ferrous nitrate used instead of sulphate.
62	25	None	5	10 "	11'65	(v. No. 58)
63	25	250	5	10 N/10 Cu(NO ₃) ₂	12'20	
64	25	None	5	10 "	11'88	Ag ₂ SO ₄ precipitated.

SERIES III.—Iodide "Sol. A" (see ante) adjusted to = N/10 Silver Solution. "B" is an Arbitrary Solution of Silver Nitrate.

Expt. No.	Sol. B. C.c.	H ₂ O added. C.c.	HNO ₃ . C.c.	Iron Solution. C.c.	Sol. A required. C.c.	Remarks.
65	25	150	2 conc.	8 Fe sulphates	18'27	
66	25	150	12 "	8 "	18'30	
67	25	150	2 "	2 "	18'25	Very quick titration.
68	25	None	2 "	Fe(NO ₃) ₃ from Fe	18'18	Very slow titration.
69	25	None	2 "	FeSO ₄ +Sr(NO ₃) ₂	18'25	Very slow titration.
70	25	None	10 "	FeSO ₄ +Sr(NO ₃) ₂	18'25	5 c.c. saturated solution NaNH ₄ HPO ₄ .
71	25	150	2 "	8 Fe sulphates	18'27	25 c.c. N/10 Pb(NO ₃) ₂ sol.
72	25	150	4 "	4 Fe nitrate sol.	18'25	
73	25	None	20 dil.	FeSO ₄ +Sr(NO ₃) ₂	18'21	
74	25	150	20 "	FeSO ₄ +Sr(NO ₃) ₂	18'27	
75	25	None	20 "	FeSO ₄ +Sr(NO ₃) ₂	18'21	
76	25	50	—	12 c.c. nitrous acid (Sol. D)	18'15	
77	25	100	—	10 c.c. nitrous acid (Sol. D)	18'22	
78	25	100	—	10 c.c. nitrous acid (Sol. D)	18'25	
79	25	100	—	5 c.c. nitrous acid (Sol. D)	18'23	
80	50	None	—	10 c.c. nitrous acid (Sol. D)	36'36	

lead salt was used, but no sulphate, ferrous and ferric nitrate solution being substituted for it. The titrations in the presence of copper nitrate, numbers 63, 64, show that this salt, as might be expected, is without influence on the result. The solution of lead contained 20·7 grms. of the metal per litre; that of copper 63·3 grms. There was accordingly about five times as much lead present as silver, or about one and a-half times as much copper.

Under Series III. a number of observations have been brought together upon the titration of larger amounts of silver, in more concentrated solution and under varying conditions, with the combined solution of starch, potassium iodide, and iodine. The deductions to be drawn from these data, in addition to those already derived in the foregoing, may be enumerated as follows:—

I. The correction for dilution does not exceed 0·02 c.c. of the N/10 solution for each 100 c.c. additional water.

II. The influence of varying speed of titration is inappreciable.

III. The influence of varying amounts of free acid (above a certain minimum), or of ferrous salt, is inappreciable.

IV. The results obtained by the use of nitrous acid as a deoxidiser are not directly comparable with those obtained when the ferrous and ferric salts are used, being lower when the solution is concentrated and higher (see Experiments 46 and 47) when dilute.

The results with the iron salts are also more constant and the reaction quicker.

V. Phosphates and lead salts are without influence.

Other experiments, not necessary to detail, show that arsenates and antimonates are without influence.

On the basis thus secured it is possible to lay down a general—

Method of Procedure.

The silver solution to be titrated should be acid with nitric acid, but ought not to contain enough of this reagent to oxidise a ferrous salt in the cold; that is, it should contain less than 5 per cent of the acid, HNO₃. It must be free from mercury and from the lower oxides of arsenic and antimony, but may contain sulphurous acid.

Add a ferrous salt in such amount that at least as much iron shall be present as silver, and an equal quantity of a ferric salt. An excess of the latter must be added if the

original solution contained sulphurous acid. If nitrous acid is present, it must first be removed by boiling.

The mixture of ferrous and ferric salts are best kept on hand in the form of sulphates which, just before use, are converted into nitrates by the addition of a moderate excess of strontium or lead nitrate solution, the last step being superfluous when the silver solution contains less than 20 m.grms. silver per 100 c.c.

The titration is to be carried on with constant stirring, and not too rapidly. Under these conditions the end reaction is never in doubt to the extent of even 0.05 c.c., provided that all reagents used are perfectly free from chlorine. A subsequent bleaching of the solution in the course of an hour or two is to be disregarded. A porcelain dish is much more suitable than a beaker for the titration, on account of the uniform white background.

Applications.

The method described is obviously applicable in many ways to residual analyses, as of chlorides, cyanides, &c., and appears especially suitable to the determination of small quantities of these substances, as in water analysis. The author intends to elaborate the process further, and desires to reserve the field for a reasonable time.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 289).

Behaviour of Amorphous Selenium in Solvents (continued). A NUMBER of experiments were then tried with amorphous selenium in various liquids, the results of which are given below:—

Aniline.—After one-half hour, perceptibly darkened; after two days, completely black.

Thiophene.—After one-half hour, no change; after three hours, crystalline without change of colour. On the following day, the material showing no further change, 0.5 c.c. quinoline was added. After fifteen minutes, the selenium had become black, but there were still glittering crystal faces to be seen. After half an hour, these had all disappeared, and the mass was uniformly black. This experiment demonstrates the power of quinoline to bring about the same change in the red crystals that it causes in amorphous selenium itself.

Pyridine.—After ten minutes, no change; after one hour, completely black.

Toluene.—After five hours, crystalline and darker in colour. No further change after seven days. After thirty days, darker in colour.

Benzonitrile.—After one day, crystalline and darkened. After thirty days more, no further change.

Benzyl Cyanide.—After one day, completely black. After fifty days, no further change.

Benzimidobutyl-ester.—After one hour, black; after fifty days, no further change.

Propyl Aldehyde.—After two days, no change; after three days, somewhat darker, but no crystals; after thirty days, very dark and crystalline.

Piperidine.—Black at once.

Amyl Nitrite.—After three days, unchanged; after thirty days, partially crystalline, colour unchanged.

Ethyl Acetate.—After one day, unchanged; after two days, somewhat darkened; after three days, almost black, without crystal faces; after thirty days, completely crystalline.

Isobutyric Acid.—After three days, unchanged; after thirty days, slightly crystalline, no change of colour.

Aqueous Ammonia.—After one hour, completely black; after fifty days, the same.

Acetophenone.—After one day, much darkened and crystalline; after three days almost black, completely crystalline; after thirty days, no further change.

Nitrotoluene.—After one day, crystalline and darkened. No further change after thirty days.

Brom-nitro-benzene (m) in Benzene.—After three hours, crystalline. No further change after thirty days.

p-β-Anisaldoxime in Alcohol.—After one day, much darkened; after two days, completely black, without crystals; after fifty days, the same.

Hydroxylamine Hydrochloride in Water.—After three days, unchanged; after thirty days, somewhat darkened in colour, not crystalline. Potassium hydroxide was then added to liberate the base; this brought about no further change in the selenium.

Dinitrobenzene (m).—After three hours, unchanged; after one day, partially crystalline; after two days, completely so. The change to the crystalline form is always accompanied by a darkening in colour, unless otherwise mentioned.

Dimethylaniline.—After one-half hour, unchanged; after three hours, crystalline; after thirty days no further change.

Nitroso-β naphthol.—After one-half hour, unchanged; after three hours, crystalline; after three days, no further change.

Urea in Alcohol.—After two days, very slightly darkened; after thirty days darkened in colour, not crystalline.

Acetone.—After three hours, darkened; after two days, black, no crystals; after thirty days, black, completely crystalline.

Ammonium Sulphocyanate in Water.—After thirty days, unchanged.

Picric Acid in Alcohol.—After thirty days, unchanged.

Triethylamine.—Begins to blacken at once; after one day, completely black; after fifty days, the same.

Phenylhydrazine.—Begins to blacken after a few minutes; after one day, completely black; after fifty days, black, minutely crystalline.

Benzylamine.—After one day, darkened; after fifty crystalline, almost black.

Propylene Bromide.—After one day, completely crystalline, red; after thirty days, much darker in colour.

Diphenylmethane.—After one day, unchanged; after fifty days, deep red, crystalline.

Ethyl Iodide.—After one day, completely crystalline, red.

Hexamethylethylamine in Alcohol.—After one day, nearly black, not crystalline; after fifty days, black.

Acetanilide in Alcohol.—After one day, very slight darkening; after fifty days, considerably darkened; about the same as in alcohol.

Potassium Hydroxide in Water.—After one day, unchanged; after thirty days, considerably darkened, not crystalline.

Ammonium Chloride in Water.—After thirty days, unchanged.

Potassium Ferrocyanide in Water.—After thirty days, unchanged.

Monomethylaniline.—After one day, unchanged; after thirty days, entirely crystalline.

Chloroform.—After one day, unchanged; after thirty days, entirely crystalline.

We see from these results that the substances studied may be divided broadly into three classes:—

1. Those which have little or no action on amorphous selenium.
2. Those which transform it into the crystalline red modification.
3. Those which transform it into the metallic modification.

In the first class we find water, hydroxylamine hydrochloride, hydroxylamine, urea, ammonium sulphocyanate, picric acid, acetanilide, potassium hydroxide, ammonium chloride, potassium ferrocyanide.

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

In the second, alcohol, benzene, thiophene, toluene, benzonitrile, propyl aldehyde, amyl nitrite, ethyl acetate, isobutyric acid, acetophenone, nitrotoluene, brom-nitrobenzene, dinitrobenzene (*m*), dimethylaniline, nitroso- β -naphthol, acetone, propylene bromide, ethyl iodide, monomethylaniline, chloroform, phenylhydrazine, benzylamine, diphenylmethane.

And in the third, quinoline, aniline, pyridine, benzyl cyanide, benzimidobutyl ester, piperidine, triethylamine, hexamethylenamine, *p*- β anisaloxime.

The substances which are most active in bringing about the change to the metallic form will be seen to be ring compounds containing nitrogen in the ring; these without exception all show the same behaviour. All the substances which cause this change are nitrogen compounds, but not by any means all nitrogen compounds are capable of causing the change; thus while aniline acts rapidly in transforming amorphous selenium into metallic, both mono- and di-methylaniline change it into the red crystalline form. It is probable that further study in this field would bring out very interesting results. Meanwhile, it looks as if it could not be a question of solubility alone which explains the difference of behaviour of these various liquids.

To determine whether amorphous red selenium would distil over in carbon disulphide to the black form at ordinary temperatures, an experiment was made in a Λ -shaped tube filled with carbon disulphide, some of the amorphous substance being placed at one end and some of the black crystals separated from sulphuric acid in the other; but, although the tube remained for several weeks, no change in the size of the black crystals could be observed. The amorphous material changed in a short time to the crystalline variety, but even this, in virtue of its higher solubility, should have displayed the phenomenon; probably the time allowed was too short.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 6th, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

THE following certificates were read for the first time:—Messrs. Andrew Charles Aitken, Rio Marina, Isola d'Elba, Italy; Thomas Stewart Barrie, 77, Sinclair Drive, Langside; John Cardew Bedwell, 65, High Street, Colchester; Herbert John Bult, 165, Brixton Hill, S.W.; Gilbert Howard Daniel, 21, Church Walk, Ulverston; Frederick George Donnan, Chemical Laboratory, University College, Gower Street, W.C.; John Alfred Emery, Cinderford, Gloucestershire; Bernard Farmborough Howard, Devon House, Buckhurst Hill, Essex; Nicholas Henry Martin, Ravenswood, Low Fell, Gateshead; Theodore Henry Page, 40, Wilson Road, Camberwell, S.E.; Thomas Slater Price, University College, Sheffield; Lionel Guy Radcliffe, 6, Alma Terrace, Old Trafford, Manchester; William Cecil Ramsden, 13, Effra Road, Rathmines, Dublin; John Talbot, Tunstall House, Harrow; James Waterhouse, Oak Lodge, Court Road, Eltham, Kent; William A. Wayland, 4, Harefield Road, Brockley, S.E.; James Scott Wilson, Bradford Street, Walsall.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. Bernard Cracroft Aston; George L. Bennett, M.A.; Hormasji N. Bilimoria, M.A., B.Sc.; Frederick Nisbet Binks; Herbert James Singleton Boyes; Theodore Ridley Burnett, Ph.D.; John Henry Cheeseright; Albert Walter Comber; Alexander Davidson; Arthur Louis William Fechtner; Willie Ludford Freeman, B.A.; William Gasson; George William Gibbings; John

Gibson; Walter Augustus Handcock; William A. Hargreaves, M.A.; George Harker, B.Sc.; Frank C. R. Hemingway; John Brownlie Henderson; Samuel Hewitt; William Henry Hewitt, B.A.; Edmund Foster Hudson, B.A.; Adolf Jappé; Humphrey Owen Jones, B.A., B.Sc.; George Washington Kilner, M.A.; Morris Charles Lamb; George Druce Lander, B.Sc.; William McCall; Hans Meyer, Ph.D.; T. Marginson Nightingale, B.Sc.; Alexander Pardy; John Paul; Ernest Vivian Pearce; Henry Ernest Stapleton, B.A.; Arthur Lambert Thornton, B.Sc.; F. Gerhard Wiechmann, Ph.D.; Walter Bourne Woodbridge; Herbert Edwards Wright, M.A.

Of the following papers, those marked * were read:—

*153. "*Santalenic Acid*." By ALFRED C. CHAPMAN, F.I.C.

The author described the preparation of a crystalline acid by the oxidation of oil of santal wood with a neutral aqueous solution of potassium permanganate. *Santalenic acid* has the formula $C_{13}H_{19}O_2$. It crystallises from dilute alcohol in transparent plates possessing a brilliant pearly lustre, is insoluble in water, but dissolves readily in all the ordinary organic solvents. It melts at 76° , boils without decomposition at 189° (corr.) under a pressure of 28 m.m., and distils with steam.

Its rotation has been determined and gives $[\alpha]_D = +18.05^\circ$.

Many of its salts have been prepared and analysed. The *methyl ester* is an oily liquid boiling at $232-234^\circ$ (35 m.m.), and has a sp. gr. = 1.0132 at $15/15^\circ$. In a 100 m.m. tube at 20° it produces a rotation of $-18^\circ 13'$.

*154. "*Ammonium Bromide and the Atomic Weight of Nitrogen*." By A. SCOTT.

During a research having for its chief aim the determination of the hydrogen to oxygen ratio by comparing the equivalents of hydrazine, ammonia, and hydroxylamine, the author found that he could not obtain the same equivalent as Stas for ammonium bromide. The value given by Stas is 98.032, whilst that of the author is 97.996, his highest value being 98.003. This would lower the atomic weight of nitrogen from 14.046 to 14.010, a number much nearer that deduced from the relative densities of oxygen and nitrogen (16:14.003).

The bromine used by Stas seems to have contained some impurity, probably platinum, as it turned greyish at 115° , and its greyness increased up to 180° ; he was unable to sublime it even in ammonia without its becoming yellow. The ammonium bromide of the author retains its whiteness at 180° , and has been sublimed in ammonia, in a mixture of hydrogen with ammonia and in a vacuum, giving the same results before and after sublimation. The silver bromide had the same composition as that of Stas (57.445 per cent of silver).

The equivalent for ammonium chloride was also determined, and found to be 53.516, as against 53.532 (Stas) and 53.486 (Marignac).

The silver used was prepared by the reduction of silver nitrate by means of ammonium formate, and was notably better than a sample prepared with the utmost care by the well-known cuprous ammonium sulphite process.

To test the purity of the silver in the severest way, the precipitated silver bromide was reduced by hydrogen, when identical results were obtained with the silver so prepared.

*155. "*Relationships of Oxalacetic Acid*." By HENRY J. HORSTMAN FENTON, F.R.S., and HUMPHREY OWEN JONES, B.A., B.Sc.

The authors have continued their investigations on the properties and relationships of free oxalacetic acid, obtained by the oxidation of malic acid in presence of ferrous iron.

The behaviour of the acid towards ammonia, aniline, hydrazine, phenylhydrazine hydroxylamine, and urea, was discussed, as well as the relation of the acid to dihydroxymaleic and dihydroxytartaric acids.

It was also shown that the hydrazone of oxalacetic acid readily loses carbon dioxide when heated with water, yielding the hydrazone of pyruvic acid, but that by a sufficient concentration of hydrogen ions this change is prevented, the hydrazone losing water instead, and giving Wislicenus's phenyl-pyrazolone-carboxylic acid; a simple method based upon these changes has been devised for comparing the "strengths" or "affinities" of various acids.

*156. "The Alkaloids of 'Corydalis cava.' The Conversion of Corybulbine into Corydaline." By JAMES J. DOBBIE, D.Sc., M.A., ALEX. LAUDER, B.Sc., and PHOTIOS G. PALLATSEAS.

Corydaline, $C_{18}H_{15}N(OCH_3)_4$, differs from corybulbine, $C_{18}H_{10}NO(OCH_3)_3$, by CH_2 , and contains four methoxyl groups, whilst the latter alkaloid contains only three (*Trans.*, 1895, lxvii., 25). The authors have now proved that corybulbine contains a hydroxyl group and forms a mon-acetyl derivative,—



By treatment with concentrated hydrogen iodide the two alkaloids yield the same phenolic derivative, $C_{18}H_{15}N(OH)_4 \cdot HI$. Corybulbine can be readily converted into corydaline by treatment with equivalent quantities of methyl iodide and potassium hydroxide in methyl alcohol solution. The artificial corydaline agrees in melting-point, solubility in various reagents, and specific rotation with the natural alkaloid. The platinichloride, ethyl sulphate, and hydriodide of the natural and artificial substances have been compared and found to be identical.

*157. "The Inversion of the Optically Active α -Tetrahydro- β -Naphthylamines, prepared by the aid of Dextro- and Lævo-bromocamphorsulphonic Acids." By WILLIAM JACKSON POPE and ALFRED WILLIAM HARVEY.

Dextro- α -tetrahydro- β -naphthylamine dextrobromocamphorsulphonate has been previously prepared from racemic α -tetrahydro- β -naphthylamine hydrochloride (*Proc.*, 1899, xv., 170); it was now shown that on treating the hydrochloride extracted from the mother-liquors with ammonium lævobromocamphorsulphonate, a precipitate of 1-tetrahydronaphthylamine 1-bromocamphorsulphonate falls, and may readily be obtained in a pure state. The new salt gives $[\alpha]_D = -86.2^\circ$ in solution in absolute alcohol, as against $[\alpha]_D = +86.5^\circ$ for its optical antipodes.

It has been shown that in preparing the benzylidene, benzoyl, and acetyl derivatives of d -tetrahydronaphthylamine, the major portion of the base undergoes optical inversion (*Proc.*, xvi., 74); on liberating the base from its salts by soda, and preparing the hydrochloride, considerable racemisation also occurs, the optically active hydrochlorides being only separable with difficulty from the mixed salts; the enantiomorphously related hydrochlorides gave in aqueous solution $[\alpha]_D = +71.9^\circ$ and -69.7° respectively. The optical inversion seems to occur during the liberation of the base by soda. d -Tetrahydronaphthylamine, d -camphor sulphonate and its enantiomorphously-related isomeride are more easily purified than the corresponding hydrochlorides; these salts crystallise with half a molecule of water, and, after drying, give in aqueous solution $[\alpha]_D = +47.7^\circ$ and -47.4° . The purest specimen of d -tetrahydronaphthylamine, obtained by treating the bromocamphorsulphonate with soda, and distilling under reduced pressure, gave $[\alpha]_D = +37.24^\circ$ in a 100 m.m. tube; this still contained about 30 per cent of the lævo-rotatory base, so that the pure dextro base would have given $[\alpha]_D = +96^\circ$ approximately.

Optical inversion attending the liberation of a base from its salts has not been previously observed, but E. Fischer has shown that leucine and glutamic acid undergo partial racemisation on benzoylation; these substances all contain the group $\begin{smallmatrix} R' \\ | \\ R'' > C < \begin{smallmatrix} H \\ | \\ NH_2 \end{smallmatrix} \end{smallmatrix}$, and the partial optical inversion is probably due to part of the base being momentarily converted into a substance containing a

group of the type $\begin{smallmatrix} R' \\ | \\ R'' > C < NH_2 \end{smallmatrix}$ during conversion of an addition compound into one containing triad nitrogen.

*158. "The Alkaloids of 'Hyoscyamus muticus' and of 'Datura Stramonium' Grown in Egypt." By WYNDHAM R. DUNSTAN and HAROLD BROWN.

In a previous paper (*Trans.*, 1899, lxxv., 72), the authors showed that *Hyoscyamus muticus* grown in India contained 0.1 per cent of hyoscyamine which is readily isolated in a pure state. Subsequently, Gadamer (*Archiv der Pharmazie*, 236, ix., 704), in a brief note, recorded the fact that the same plant grown in Egypt contains more than ten times this quantity. Through the kindness of Mr. E. A. Floyer, the authors have been enabled to examine a specimen of the plant from Egypt. They find it to be much richer in hyoscyamine than the sample of Indian growth previously examined. The seeds furnished 0.87 per cent, and the stems and leaves 0.59 per cent. It remains to be determined whether the Indian plant is always poorer in alkaloid or whether it was a peculiarity of the sample examined.

The authors call attention to the Egyptian plant as an important source of the alkaloid hyoscyamine.

Datura Stramonium grown in the Egyptian desert also contains hyoscyamine, unaccompanied by other atropaceous alkaloids, to the extent of 0.35 per cent.

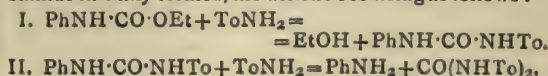
An abundant supply of either plant could be obtained from Egypt.

159. "Interaction of Urethanes and Primary Benzenoid Amines." By AUGUSTUS EDWARD DIXON, M.D.

Manuelli and Comanducci have described (*Gazz.*, 1899, xxix., ii., 142), as phenylparatolylcarbamide, $PhNH \cdot CO \cdot NHTo$, a substance they obtained by heating phenylurethane with paratoluidine; they give its melting-point as $259-260^\circ$, and confirm the formula by a complete analysis. These chemists have apparently overlooked the descriptions of phenylparatolylcarbamide given by Huhn (*Ber.*, 1886, xix., 2408), Goldschmidt and Meissler (*Ber.*, 1890, xxiii., 273), and the author (*Trans.*, 1895, lxvii., 562), who record the melting-point as 211° , 211° , and $212-213^\circ$ respectively; Paal and Vanvolxem (*Ber.*, 1894, xxvii., 2426), give its melting-point as 202° .

It occurred to the author as just possible that Manuelli and Comanducci's compound might be a "labile" form of the symmetrical carbamide, for instance, $PhN:C(OH) \cdot NHTo$; in order to find out if the discrepancy noted above might be thus explained, the interaction of certain urethanes and aromatic bases was investigated.

Phenylurethane and paratoluidine, when heated together, yielded aniline and a crystalline solid; the latter consisted of a main portion melting at $260-261^\circ$, which was proved to be, not phenylparatolyl-, but diparatolylcarbamide, along with a small quantity of phenylparatolylcarbamide melting at $213-214^\circ$. It is suggested that the production of diparatolylcarbamide is due to the expulsion of aniline by toluidine from the phenyltolylcarbamide initially formed, the actions occurring as follows:—



Aniline heated with paratolylurethane gave a solid product which consisted mainly of phenylparatolylcarbamide, m. p. $213-214^\circ$, with only a small quantity of a substance melting at about $256-257^\circ$, probably diparatolylcarbamide.

From orthotoluidine and phenylurethane, aniline always was liberated, the solid product being a mixture, from which were separated (1) vitreous prisms, melting at $249-250^\circ$ (diorthotolylcarbamide), and (2) woolly-looking clumps of needles melting at $203-204^\circ$; these were nearly pure phenylorthotolylcarbamide. The latter compound, when prepared by aging with silver n.trate on the corresponding thiocarbamide, or from phenyl isocyanate and orthotoluidine, melted at $207-208^\circ$.

It seemed therefore not improbable that the *s*-phenyl- α -naphthylcarbamide prepared by Manuelli and Comanducci from phenylurethane and α -naphthylamine, and stated to melt at about 277–278°, might prove to be really di- α -naphthylcarbamide; this interaction was therefore re-examined. Phenyl- α -naphthylcarbamide was prepared in two distinct ways and found to melt at 222–223°. Immediately after melting it re-solidifies, re-melting about 20° higher; the cause of this behaviour has not yet been investigated.

When phenylurethane was heated with α -naphthylamine as described, much aniline was formed, together with a solid mixture, which, when boiled with alcohol, left di- α -naphthylcarbamide, which is nearly insoluble, and melts rather indistinctly at 286–287°; from the extract a small quantity of a substance was deposited which crystallised from alcohol in woolly-looking needles. This melted at about 221°, re-solidifying immediately, as described above, and evidently consisted of phenyl- α -naphthylcarbamide.

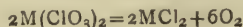
Manuelli and Comanducci also obtained from normal amylamine and phenylurethane a colourless solid, melting at 238°, which they regard as *ab*-amylphenylcarbamide, but which the author thinks is probably carbanilide.

160. "The Decomposition of Chlorates. Part III. Calcium Chlorate and Silver Chlorate." By WILLIAM H. SODEAU, B.Sc.

When calcium chlorate is decomposed slowly about 0.6 per cent of its total chlorine is evolved, whether the pressure be 760 m.m. or 4 m.m., but the proportion exceeds 2 per cent when the decomposition under atmospheric pressure is rendered violent. As the proportion of free chlorine is independent of the pressure of the gaseous products, the calcium chloride in the residue is not produced by the action of chlorine upon oxide first formed.

When silver chlorate is heated to about 350° it explodes with a yellow flash, about 7 per cent of its chlorine accompanying the oxygen. When slowly decomposed the influence of pressure is even greater than in the case of lead chlorate (*Trans.*, 1900, lxxviii., 718). At atmospheric pressure only 0.2 per cent of its chlorine remains free, but 22.6 per cent is obtained at 2½ m.m. pressure, and more than 36 per cent should be obtained if the action between chlorine and silver oxide could be completely eliminated.

It is concluded that oxygen and chlorine are produced during the slow decomposition of either chlorate by two simultaneous independent reactions represented by the equations—



and—



(where M = Ca or Ag₂). With calcium chlorate the "chloride" decomposition proceeds at about 180 times the rate of the "oxide" decomposition, whilst with silver chlorate the ratio is less than 18:1.

The probability of the "oxide" decomposition being endothermic suggests an explanation of the increase of chlorine in rapid decomposition at high temperature.

Silver chlorate differs from the chlorates of potassium, barium, and calcium in his highly explosive nature, and in the occurrence of an extremely strong secondary action between chlorine and the oxide, but resembles the chlorates of potassium, barium, calcium, and lead, in that no free chlorine is produced by displacement from the chloride.

161. "On Iron Nitride." By G. J. FOWLER, M.Sc.

Nitride of iron was prepared by three different methods: by the action of ammonia on (a) finely divided iron, (b) ferrous chloride and bromide, (c) iron amalgam. Of these methods (a) is the most convenient. The substance was found to correspond to the formula Fe₂N. The temperatures of the formation of iron nitride in ammonia and of its decomposition in hydrogen are identical. These results confirm the conclusions of Stahlschmidt. Heated

in a current of nitrogen, iron nitride begins to decompose at about 600°; it is slightly magnetic; its specific gravity is 6.35.

When oxidised in air or oxygen, only traces of oxides of nitrogen are produced; heated in a current of air, the substance begins to be converted into ferric oxide and nitrogen at about 200°. It takes fire in chlorine ether spontaneously, or when slightly warmed, ferric chloride and nitrogen being formed, but no trace of nitrogen chloride. It is only slowly attacked by bromine, the action probably being due to the presence of hydrobromic acid in the bromine as an impurity. An ethereal solution of iodine has no action on it.

Dilute hydrochloric and sulphuric acids yield the corresponding ferrous and ammonium salts, hydrogen being liberated according to the following equation: $2\text{Fe}_2\text{N} + 6\text{H}_2\text{SO}_4 = 4\text{FeSO}_4 + 2\text{NH}_4\text{HSO}_4 + \text{H}_2$.

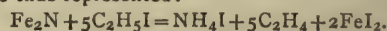
The simultaneous action of hydrogen peroxide and sulphuric acid is not distinguishable from that of the acid alone. Nitric acid acts only slowly on the nitride even when strong; the products formed vary with the concentration of the acid.

Gaseous hydrochloric acid begins to attack the nitride at about 220°, and at 350° the reaction becomes rapid, the substance being completely converted into ferrous chloride and ammonium chloride. Gaseous hydrogen sulphide has a precisely similar action at 200°.

Nitric oxide acts similarly to oxygen, and converts the nitride into oxide, the reaction beginning at about 120°, and becoming rapid at 170°. Carbon dioxide oxidises the nitride at about 530°. On heating the nitride in steam at 100°, ammonia is very slowly formed. The nitride heated with sodium and carbon yields sodium cyanide.

It was thought that phenol might act on nitride of iron in the same way as dilute acids, but the two substances do not react.

On heating with ethyl iodide in a sealed tube to 200–230°, gas is produced consisting chiefly of olefines, with a trace of paraffins, but no amines. The reaction may probably be thus represented:—



(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, December 14th, 1900.

Principal O. J. LODGE, President, in the Chair.

By invitation of Prof. Rücker, this meeting was held in the Physical Laboratory of the Royal College of Science.

A paper "On Electric Inertia and the Inertia of Electric Convection" was read by Prof. A. SCHUSTER.

Calculations of self-induction are based on the assumption that the currents which traverse a conductor fill it continuously, the flow being treated as that of an incompressible liquid. The assumption is generally recognised not to hold in the case of electrolytes where electricity is conveyed by a number of irregularly distributed ions. In the immediate neighbourhood of such an ion the magnetic field is many times greater than that calculated on the supposition of continuous distribution, and hence the total magnetic energy is under-estimated. What is universally recognised in the case of electrolytes must also be conceded when the current is conveyed by a gas, and the idea is gaining ground that even in solid conductors the current consists of positive and negative electrons moving with different velocities. It is the object of the paper to calculate the additional terms which become necessary for the evaluation of self-induction, and to discuss the possible cases in which the corrections may effect experimental results. The mathematical investigation shows that it is necessary to add a correcting term containing a quantity which may conveniently be called electric inertia. The

author has calculated the numerical value of this quantity in the case of a solid conductor, and finds it to be about 2×10^{-13} C.G.S. units. It is of the dimensions of a surface. The experiments of Hertz have proved that if electric inertia exists it must be less than 18×10^{-8} . In the case of liquids and gases the electric inertia of the moving ions becomes much more important, and the calculation of self-induction by the ordinary processes gives erroneous results. The introduction of a term representing inertia alters the general equations of electric motion, and the author has applied his modified theory to Leyden jar discharges, the electrodeless discharges of J. J. Thomson, and the electro-magnetic theory of light. In the case of electrodeless discharges in a vacuum globe it is suggested that the absorption of energy may not only be due to the conductivity of the gas, but also to the inertia which it possesses.

A paper "On Magnetic Precession" was then read by the same author.

The most delicate method of investigating the influence of electric inertia is based on the electromotive forces introduced by the motion of conductors carrying electric currents. If electricity behaves like a body possessing inertia, the rotation of a body through which currents pass should affect the flow of these currents in the same manner as the earth's rotation affects the direction of currents of air. If the earth's magnetism is due to electric currents it is interesting to see if the effects of inertia can explain the secular variation. The investigation shows that a magnetic precession of the character of the secular variation would be produced, but that the precession would be very much slower than the variations actually observed. The subject is worked out mathematically, dealing first with the case of currents in a spherical shell, and then extending the result to the case of a solid sphere. The calculated period of a cycle comes out as 7×10^{14} years. If the currents are confined to a thin slice of the earth the time would be reduced to about 14×10^6 years. To produce the actual period of the secular change the current sheet would have to be of molecular dimensions. This suggests the possibility of the phenomenon of secular variation being rather of a molecular than a molar character.

Prof. RÜCKER congratulated the author upon his attempt to solve the problem of terrestrial magnetism, and expressed the hope that further calculation would throw more light upon this difficult subject.

Mr. BLAKESLEY asked if the time of the secular variation would be altered if the interior of the earth were liquid or solid.

The CHAIRMAN observed that the precession was rapid in the case of a thin layer of gas, and mentioned J. J. Thomson's notion that the electrons were thrown off by centrifugal force, and formed a molecular layer. Hertz, in his experiments on electricity, had looked for material inertia besides electromagnetic inertia. In the present theory the distinction disappears, and there is only one inertia, and that electromagnetic.

Prof. AYRTON said if the two forms of inertia were electromagnetic, he would like to know why in detecting the second form it was necessary to associate it with an absorption of energy as in the case of an electrodeless discharge. In the case of ordinary self-induction there is no absorption of energy, and if there is absorption in the second form, and if they are both electromagnetic, he would like to know the difference between the two.

Prof. SCHUSTER, replying to Mr. Blakesley, said that if the interior of the earth were treated as liquid the period of the cycle would be about one hundred times less. In reply to Prof. Ayrton, he said he had only cited one experiment to show that a phenomenon explained by the gas being a good conductor could also be explained by its electric inertia. It was impossible to say in general whether self-induction caused an absorption of energy or not.

Prof. A. W. RÜCKER read a paper "On the Magnetic Field produced by Electric Tramways."

Taking the case of a tramway in which the current flows along a trolley wire from the power house, and returns partly through the rails and partly as earth currents, the author has shown that the vertical disturbing force at any point is due to the currents in the feeders and rails, and that the earth currents affect the horizontal force only. Experiment shows that it is chiefly the vertical force instruments which are affected by the establishment of an electric railway, and since this disturbance is due to the wires and rails it is impossible for an observatory to be protected by rivers or other natural features of the district. A preliminary investigation is based on the assumption that the trolley wires and rails are insulated conductors, and that a fraction of the whole current returns along the rails to the generator. The effect of the railway at a distant point is due to the difference of the current in the trolley wire, and the hypothetical uniform rail current, the effect of which at the point considered is equivalent to the actual rail current, which varies from point to point. It is shown that the disturbance increases with the length of the tramway, and for a tramway of given length the disturbance is a maximum at points on a line perpendicular to and bisecting it. Experiments made at Stockton on the magnitude of the disturbing force gave, with the vertical force instrument, a leakage of 16.3 per cent, and with the horizontal force instrument a leakage of 15.9 per cent; a fairly close agreement. The assumption that the terminals of the line are above and below the average potential of the earth by the same amount respectively, and that the leakage at any point is proportional to the potential difference between the rail and the earth, leads to the ordinary theory of a Fourier bar. This more accurate assumption has been developed and applied to the results obtained at Stockton. The leakage as calculated from the amperes and volts comes out as 20 per cent. The calculation of the disturbing vertical force gives 10.5×10^{-3} C.G.S. units, which is in fair agreement with the value 7×10^{-3} actually observed. In conclusion, it is pointed out that for practical purposes it is sufficient to deal with the average return current through the rails, the formulæ for which are quite simple.

Dr. R. T. GLAZEBROOK read some "Notes on the Practical Application of the Theory of Magnetic Disturbances by Earth Currents."

In this paper the author has thrown the extended formula obtained by Prof. Rücker in the previous paper into a workable form, and has tabulated numbers which show at what distances the disturbances are negligible for tramways of different lengths.

Prof. R. THRELFALL exhibited a "Quartz-thread Gravity Balance."

Prof. Threlfall gave a short description of this instrument, which has been described in full elsewhere. He drew attention particularly to its accuracy and portability.

Mr. SIMPSON asked how far the fibre had been calibrated, and if the instrument would be reliable at the freezing-point of mercury.

Dr. GLAZEBROOK asked how far the instrument was suitable for Antarctic expedition work. He drew attention to the difficulty of calibrating a new fibre should one get broken in the field.

Mr. APPEYARD suggested the use of a bath kept at constant temperature with a thermostat.

Prof. S. P. THOMPSON suggested a Special Meeting to discuss the Physics of the Antarctic Expedition.

Prof. THRELFALL said that there was no difficulty in measuring the relation between temperature and coefficient of stiffness down to very low temperatures. A more difficult matter is the coefficient of temperature of the instrument. Shrinkage of the instrument as a whole affects both the fibre and the spring which supports it. The difficulty of a broken fibre in the field can be got over by taking two or three instruments. Working with a

thermostat is useful in a laboratory, but decreases the portability in exploration work.

Mr. WATSON then exhibited a set of half-seconds pendulums. In these pendulums special attention is paid to the stability of the support. They are covered by a hood from which the air can be exhausted so that the logarithmic decrement is diminished. The motion of the pendulums is shown by rays of light reflected from right-angled prisms attached to them, and the period of oscillation is determined by the method of coincidences. For this purpose an accurate astronomical clock is used, and the observations are made continuously between two time signals. An accuracy of one part in a million is attainable.

In reply to Prof. THRELFALL, Mr. Watson said that the knife-edges were on the pendulums and not on the supports.

The Society then adjourned until January 25th, 1901.

NOTICES OF BOOKS.

Quantitative Chemical Analysis. Adapted for use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., Lond., and J. B. COLEMAN, A.R.C.Sc., Dublin. Fifth Edition. London: J. and A. Churchill. 1900. Pp. 592.

THE plan adopted in the previous editions of this book is still adhered to, and endeavour has been made by repeated revisions to eliminate errors, and to include every improvement and useful addition.

An appendix has been added to the present edition, containing descriptions of a modification of the usual method of determining melting-points, of a special apparatus for the rapid filtration and ignition of precipitates by using a perforated crucible lined with asbestos-felt, and an improved form of condenser for use in the distillation of liquids. It also contains descriptions of the following processes:—The determination of nickel by electrolysis, the titration of soluble cyanide by standard iodine solution, the determination of titanium in titaniferous iron ores, and the estimation of nickel and aluminium in steel.

The atomic weights, page 528, used in this volume, are those given for the year 1900, by the Atomic Weights Committee of the German Chemical Society; in this table we note the elements selenium and tellurium. This termination evidently refers to their non-metallic state, but it seems an unnecessary alteration of name.

An Epitome of the Law and Practice connected with Patents for Inventions. By JAMES JOHNSON, Barrister-at-Law, and J. HENRY JOHNSON, Assoc. Inst. C.E. Third Edition, carefully revised. London: Longmans, Green, and Co. New York and Bombay: Stevens and Sons, Limited. 1900. Pp. 164.

THERE are also included in this volume a reprint of the Patents' Acts of 1883, 1885, 1886, and 1888, and the official rules, as well as a summary of foreign and colonial patent laws.

The alterations made from time to time in the law have been carefully shown, and a statement of the procedure to be followed on applying for a patent is given.

Notwithstanding its small size the book will be found to contain a sufficiently adequate outline of the law in its present state.

In consequence of the reduction of fees, and the simplification of procedure since the Act of 1883 came into force, the annual number of applications for patents has considerably increased, and we have no doubt that this book will be of much use in showing in plain language the principal rights, duties, and liabilities of applicants and patentees.

CORRESPONDENCE.

ARSENIC IN BEER.

To the Editor of the Chemical News.

SIR,—I have read Mr. Estcourt's article as to the interference of calcium bisulphite with Marsh's test with interest. In common with most public analysts I have had lately a large number of samples of beer to test for arsenic. My process has been to boil off alcohol and carbonic acid, to alkalis with caustic soda, to evolve hydrogen from sheet aluminium, and to pass the gas through a c.c. of silver nitrate solution in a test-tube.

The process will readily detect 0.01 m.grm. of arsenious acid in 100 c.c. of beer. I have proved that the acid sulphites in no way interfere with the test. The only precautions are the obvious ones of control experiments, and the regular slow evolution of the gas.

The samples are put on in the evening, and examined the following morning. An accurate quantitative estimation of arsenic involves, more or less, complete destruction of organic matter, but as a *preliminary* test the aluminium process is simple, and enables a large number of samples to be tested in a day.—I am, &c.,

A. WYNTER BLYTH.

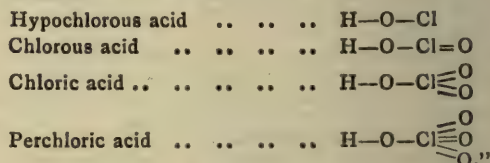
The Town Hall Laboratory,
St. Marylebone, December 15, 1900.

VARIABLE VALENCY.

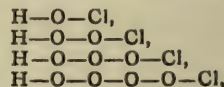
To the Editor of the Chemical News.

SIR,—As a student of elementary chemistry, I have been much puzzled by the following passage in Roscoe's "Lessons" (1888 edition, p. 158):—

"It would appear that chlorine is a monad in hypochlorous acid, a triad in chlorous acid, a pentad in chloric acid, and a heptad in perchloric acid. This is rendered evident by the following graphic formulæ:—



Granting that such variable valency is a fact, Roscoe is certainly incorrect in saying that it is "rendered evident" by these formulæ. No reason is given for not writing them thus:—



representing chlorine as a monad all through the series.—I am, &c.,

W. F. DUNTON.

26, Tregothnan Road, Stockwell, S.W.,
London, December 5th, 1900.

SIMPLE TEST FOR ARSENIC.

To the Editor of the Chemical News.

SIR,—A want is especially felt at the present time of some quick and ready qualitative test for arsenic. I venture to recommend the following slight modification of Fleitmann's test, which has the advantage of being, like Reinsch's test, applicable in the presence of organic matter, while it is as delicate as, and much simpler than, Marsh's test:—

Place in a test-tube about 6 or 8 c.c. of the liquid to be tested, add about a grm. of solid potassium hydrate, and heat the mixture nearly to boiling. Drop into the solution a bit of aluminium foil, and lay on the mouth of the tube a small piece of filter-paper moistened with solution of silver nitrate. If arsenic is present, hydrogen arsenide will be evolved, and will decompose the silver nitrate, which will turn black owing to formation of metallic silver.

The presence of compounds of sulphur or of phosphorus does not interfere with the above test, since they are retained by the strongly alkaline solution, and no hydrogen sulphide or phosphide is formed.—I am, &c.,

H. G. MADAN.

ANALYSIS OF FERRO-SILICON AND SILICO-SPIEGEL.

To the Editor of the Chemical News.

SIR,—Having read with interest the article on the above subject by Messrs. Ibbotson and Brearley (CHEMICAL NEWS, vol. lxxxii., p. 269), I venture to make a few remarks, as one who has had not an inconsiderable experience in the analysis of these alloys. My experience coincides with that of Hogg, when he states that the silica retains ferric oxide when the alloy is dissolved in aqua regia and evaporated to dryness, &c. But this retention may be entirely obviated by the addition of from 5 to 10 c.c. strong H_2SO_4 when the solution in aqua regia is complete, and then evaporating until the H_2SO_4 fumes; cool, dilute with water, filter, &c. This method is more especially applicable to silico-spiegels. The silica comes out snow-white, and leaves no residue after HF.

As regards ferro-silicon, especially with the higher percentages of silicon, the aqua regia method of solution is very far from perfect. It is difficult, if not impossible, to obtain the silica so clean as would be the case if the following method were adopted:—Take 1 grm. of the finely divided alloy in a dry beaker, add from 5 to 10 c.c. pure bromine, then about 20 c.c. hydrochloric acid (it is a remarkable fact that the bromine should be put on first, then the HCl; also that the beaker is to be dry). Place in a moderately warm spot on the hot plate. Complete solution will be effected in from fifteen to twenty minutes; then add cautiously about 5 c.c. HNO_3 ; copious fumes of bromine come off. When these cease, add H_2SO_4 , 5 to 10 c.c., as in case of silico-spiegels, and evaporate to fuming; cool, dilute filter, &c., as usual. The resulting silica is perfectly pure and leaves no residue after HF. In both cases care is necessary in burning off the residues, as the silica is in a very finely divided condition, and is liable to fly out of the crucible if hurried in the drying and ignition.—I am, &c.,

T. H. BYROM.

Laboratory,
Wigan Coal and Iron Company,
Wigan, December 13, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 22, November 26, 1900.

The Existence of Nitrides of Neodymium and Praseodymium.—H. Moissan.—Referring to a paper published in the last number of the *Comptes Rendus* on the subject of the nitrides of the rare earths, the author states that, in his paper of October 15th, 1900, he announced the

existence of two nitrides of neodymium and praseodymium prepared by the action of ammonia-gas on the carbides of the above metals at a temperature of 1200°.

Cryoscopic Researches.—Paul Chroustchoff.—From the results of a large number of researches on the subject of the lowering of the freezing-point of water containing in solution salts and organic substances, the author finds many contradictions, and so undertakes the same research, substituting for the mercury thermometer Callendar and Griffith's electric thermometer, which was slightly modified to meet the required conditions. From the numbers obtained he concludes that—(1) There exist solutions in which the coefficient of the lowering of the freezing-point does not vary with dilution, as NaCl, within the limits of the experiment, but that of KBr diminishes slightly with dilution. (2) For other solutions, this coefficient increases in a very marked manner in certain cases, as K_2SO_4 solution, or in a very slight degree as cane-sugar solution. (3) The results agree, at least in their general character, with those of M. Ponsot.

New Method of Estimating Arsenic.—O. Ducru.—In a weak ammoniacal solution, rich in ammonia salts, arsenic acid can be completely precipitated by cobalt salts. This reaction can be employed in estimating arsenic. The conditions necessary are very simple: the cobalt must be in decided excess, about one and a-half times the theoretical quantity, and the solution should be slightly ammoniacal. If it contains in the free state 1.5 per cent of its volume of 20 per cent ammonia, the conditions for the formation of mono-ammonic arsenate of cobalt are fulfilled. Practically, to allow for loss during heating, about 3 per cent should be taken. It is also necessary to charge the liquid with ammonium chlorohydrate, about 100 grms. per litre, though in certain cases it is preferable to use acetate.

A General Method of Separating the Metals which accompany Platinum.—E. Leidié.—The commercial extraction of platinum and iridium from their minerals leaves a residue which contains a number of rare metals, such as osmium, ruthenium, palladium, and rhodium. The author devises a method of separating these metals from one another, based on the properties of their nitrites.

Direct Combination of Hydrogen with the Metals of the Rare Earth Group.—Camille Matignon.—The author finds that neodymium, praseodymium, and samarium combine directly and rapidly with hydrogen. Thorium, cerium, and lanthanum are already known to absorb hydrogen with the same rapidity. All the hydrides thus formed are dissociable. The method which served to establish the above facts at the same time allows of the measurement of heterogeneous dissociation pressures of these hydrides in a very simple manner.

Some Chlorobromides of Thallium.—V. Thomas.—The author prepared a number of mixed salts either by the action of variable quantities of bromine on thallous chloride or by the action of bromine on the products of decomposition of chlorobromides under various conditions. The first salt examined was the chlorobromide $\text{Th}_3\text{Cl}_2\text{Br}_4$, which was prepared in a well crystalline form by treating thallous chloride with excess of bromine, and evaporating the solution in a vacuum over sulphuric acid. The crystals thus formed are yellow, and apparently undergo a change on exposure to air. They are decomposed by water.

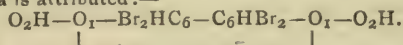
Cadmium Selenide.—M. Fonze-Diacon.—The author prepares a crystallised cadmium selenide, SeCd , which is rhombohedral and isomorphous with zinc selenide obtained under the same conditions. He also shows the existence of cadmium chloro-, bromo-, and iodo-selenides. The iodoselenide, which is yellow in the presence of water, becomes bright orange-red on desiccation, and is very stable.

Detection of Metals contained in very small Quantities in Mineral Waters.—F. Garrigou.—The results obtained up to the present time during the ordinary

analyses of mineral waters on 1 or 2 litres of water, give no idea of the number and the quantity of metals which are contained in these waters, transported from the deep soils. If 10 to 20 litres are used and the most delicate tests are applied, the presence of various metallic radicles can be established which ordinary analysis fails to identify. The author thus examined water from Eaux-Bonnes, Bagnères-de-Bigorre, Bourboule, and Barèges, and confirmed his old analyses made on thousands of litres. He intends to show that this method of procedure allows also of the separation of the various organic matters from water (acids and alkaloid).

Nitration of Bi-substituted Derivatives of Benzene.—Ch. Cléz.—Noëling and others have fixed certain rules relating to the nitration of mono-substituted derivatives of benzene, and from a study of these the author formulates a series of rules for bi-substituted benzene derivatives, which he enunciates as follows:—(1) The bi-substituted benzene derivatives enclose the basic group NH_2 (acetyl) or NR_2 . (2) The bi-substituted benzene derivative is a phenol (OH being feebly acid). (3) The bi-substituted benzene derivative contains a neutral group, Cl or CH_3 ; and (4) it contains the two acid groups COOH and NO_2 .

Action of Nitric Acid on Tribromated Gaïacol.—H. Cousin.—When tribromated gaïacol is treated with nitric acid, two molecules of gaïacol lose each an atom of bromine, and thus form a derivative resulting from the joining of the two benzenic radicles. At the same time the two molecules of gaïacol are saponified and transformed into phenolic functions. Nitric acid then acts as an oxidiser, and removes H_2 from two phenolic oxyhydrils OH; thus a quinone is formed to which the following formula is attributed:—



Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxiii., No. 13.

The Lower Oxides of Phosphorus.—M. Besson.—A controversial paper, traversing the statements recently made (*Lieb. Ann. Chem.*, cccx., 45) by MM. Michaelis and Pitzch.

Wet Reaction by which Mercuric and Mercurous Iodide can be obtained directly in the Crystalline Form.—F. Bodroux.—Already noticed.

Partial Synthesis of Left-handed Erythrite.—L. Maquenne.—This substance is obtained by the hydrolysis of erythrose acetamide by means of boiling dilute sulphuric acid; it is then neutralised with soda, evaporated in vacuo, and shaken up with 3 per cent sodium amalgam, keeping the liquid slightly acid to prevent the isomerising action of an excess of alkali. After about an hour the solution is carefully neutralised, concentrated on the water-bath until crystallisation commences, taken up with alcohol to separate the insoluble sulphates of sodium and ammonium, evaporated down again, and finally taken up with four or five times its volume of absolute alcohol; it is then saturated with hydrochloric acid gas, and finally treated with a large excess of benzoic aldehyde, which immediately precipitates the erythrite in the state of insoluble acetal. This latter is collected after twenty-four hours, washed with alcohol at 50° , and hydrolysed by boiling for about half-an-hour with ten times its weight of alcohol containing three or four hundredths of sulphuric acid. When the solution is complete, the alcohol and the benzoic aldehyde are driven off with a current of steam; it is then neutralised with chalk, evaporated on the water-bath, and taken up with boiling absolute alcohol. This last solution soon deposits crystals of pure *l*-erythrite.

Researches on Symmetric Diphenylcarbazide. Organo-Metallic Compounds of Diphenylcarbazone.—P. Cazeneuve.—Already noticed.

Some Compounds of Diantipyrine-methane (Formopyrine).—G. Patein.—Ten grms. of iodine and 10 grms. of formopyrine are each dissolved in 150 to 200 c.c. of alcohol at 95° ; the solution of iodine is poured drop by drop into the solution of formopyrine while constantly stirring; fine needles soon begin to appear in the liquid, and they increase with every addition of iodine; after standing for some hours in a cool place the crystals are collected on a filter-paper, washed with alcohol at 95° , and dried in the air. They have the appearance and colour of iodine, but are stable at a fairly high temperature, and give off no vapour. Analysis shows that this body contains 1 molecule of formopyrine combined with 4 atoms of iodine. Formopyrine will not combine directly with pyrocatechin, but if treated together at 100° , in the presence of sulphuric acid, a crystalline body is obtained. In the same way formopyrine and hydroquinone give a colourless mass of crystalline needles, fusible at $218-220^\circ$. Formopyrine and resorcinol also give colourless crystals, fusing at 220° .

MISCELLANEOUS.

Royal Institution.—On Thursday next, December 27, at three o'clock, Sir Robert S. Ball, F.R.S., will deliver the first of the Christmas Course of Lectures, specially adapted to young people, at the Royal Institution, his subject being "Great Chapters from the Book of Nature." The remaining Lectures will be delivered on December 29, and January 1, 3, 5, 8, 1901.

Qualitative Separation of Antimony and Tin.—G. Bornemann.—When we add a quantity of soda-lye to a solution of chloride of antimony, until the precipitate formed is re-dissolved, and then treat this solution with a sufficient quantity of phosphate of sodium and boil, there is no precipitate formed as long as the liquid is warm. A solution of stannic chloride, subjected to the same treatment, loses nearly the whole of its tin in the form of a dense, white precipitate. But on treating a mixture of chloride of antimony and chloride of tin in the same manner, the precipitate of stannic phosphate always carries down a certain amount of antimony. However, the filtrate is free from tin, and sulphuretted hydrogen only causes an orange precipitate, or cloudiness of sulphide of antimony. These facts have enabled me to devise the following process:—The liquid to be examined should contain all its tin in the form of stannic chloride. We then add a drop of phenolphthalein, or litmus, and enough soda to obtain a clear solution with a strongly alkaline reaction. The solution thus obtained is treated with a sufficient excess of a solution of phosphate of sodium, and the whole made slightly acid with nitric acid. It is then boiled, and left to stand for some time. If no precipitate is formed it is diluted and heated over again. The continued absence of a precipitate shows the absence of tin. The phosphate of tin is thrown on a filter, and the filtrate treated with sulphuretted hydrogen.—*Zeitschrift für Angewandte Chemie*, xii., p. 635.

MEETINGS FOR THE WEEK.

THURSDAY, 27th. { Royal Institution, 3. (Christmas Lectures to
SATURDAY, 29th. { Young People). "On Great Chapters from
the Book of Nature," by Sir Robert Stawell
Ball, D.Sc., LL.D., F.R.S.

TO CORRESPONDENTS.

W. L. Watson.—See "Coal-tar and Ammonia," by Dr. George Lunge (third edition), published by Gurney and Jackson, 1, Paternoster Row.

THE CHEMICAL NEWS.

VOL. LXXXII., No. 2144.

THE DETECTION OF ARSENIC.

By ALFRED H. ALLEN.

THE recent correspondence in the papers, emanating chiefly from chemists who have been concerned in the deplorable epidemic of arsenical poisoning in Lancashire, has led to some interesting disclosures. Especially curious are the statements made respecting the delicacy of Marsh's test for arsenic, and its suitability for examining beer for that element.

Mr. William Kirkby states that it is doubtful whether Marsh's test, under the most favourable conditions, will indicate less than one grain of arsenic in 100,000 parts, or say about three quarters of a grain per gallon of beer. This astounding experience may be contrasted with the statement of Mr. Frank Scudder—apparently rather on the dubious authority of the text-books—as a result of his personal experience, that a mirror on a porcelain basin, in which you can see the reflection of your face, can be obtained from $\frac{1}{16}$ th of a gallon of a liquid containing one part of arsenious oxide in 700,000. But Mr. Scudder does not in practice employ these quantities, preferring to operate on not less than 1 litre of the beer.

Mr. William Thomson finds that, working on 150 c.c. of the beer, an amount of arsenic equal to one-hundredth of a grain of As_2O_3 can be detected with certainty by Marsh's test. He attributes the difficulty many analysts experience in detecting arsenic in beer to the imperfect or unsuitable methods they adopt to destroy the organic constituents of the liquid.

Mr. Chas. Estcourt has done good service by reminding analysts of the frequent presence of sulphites in beer, and of the fact that such beer will not give an arsenical mirror with Marsh's test. It is well known that sulphites evolve sulphuretted hydrogen when treated with zinc and dilute acid, and if this is produced in sufficient amount it may cause complete conversion of the arsenic into sulphide in the evolution-flask, and so remove it from the sphere of action. But I have in mind a case in which the material (burnt pyrites), when examined by Marsh's test, gave a yellow deposit of arsenious sulphide just beyond the heated part of the tube. At any rate, it is clear that sulphites interfere with the employment of Marsh's test, and should be previously removed. Mr. Estcourt effects this by boiling the beer for some time with acid before adding the metal. This appears to me an uncertain and tedious method, and I effect the immediate destruction of any sulphites by adding a little bromine-water, or potassium permanganate, to the acidulated beer. I prefer bromine-water, as it does not act on the organic matter so readily as permanganate, and the excess can be readily removed by a few minutes' boiling. Whichever plan be adopted, the arsenic is oxidised to the arsenic state, and some time elapses before the liquid will evolve arsenical hydrogen in Marsh's apparatus. This inconvenience I avoid by adding a few drops of a solution of cuprous chloride in hydrochloric acid to the contents of the evolution-flask. This reagent instantly reduces the arsenic to the arsenious state, and arsenical hydrogen is evolved almost immediately. The use of cuprous chloride has the additional advantage that it results in the formation of a copper-zinc couple, and the evolution of hydrogen is much facilitated.

A working difficulty in the examination of beer by Marsh's test is met with in the persistent frothing of the liquid; this may be in a great measure overcome by pre-

viously boiling the beer till it is reduced to about half its original bulk. Even then a capacious flask is necessary. Oxidation of the organic matter also mitigates the difficulty.

Mr. Kirkby has described his method of applying Gutzeit's well-known mercuric chloride test for arsenic. It is undoubtedly very delicate, and is used by Mr. Kirkby on 3 c.c. (!) of the beer. But the test does not appear to present any other advantages, and a yellow stain on a piece of filter-paper does not appeal to my mind in the same way as an arsenical mirror, or the formation of crystals of characteristic form. Messrs. Paul and Cownley fully endorse this view, and consider that to obtain a satisfactory result with the mercuric chloride test is out of the question.

I have recently had a considerable number of samples of beer to examine for arsenic, and find Reinsch's test to be the most satisfactory. I purify the hydrochloric acid employed by distilling off about one-tenth; this fraction containing the minute trace of arsenic originally present. I operate, as a rule, on 100 c.c. of the beer, and as a preliminary treatment to eliminate sulphites, add hydrochloric acid and a little bromine-water, and boil the liquid for a few minutes. To obviate the difficulty caused by the fact that arsenic acid only responds to Reinsch's test after prolonged boiling, and in presence of much acid, a little solution of cuprous chloride in hydrochloric acid is next added, which reduces the arsenic to the arsenious condition. On now introducing about one square centimetre of copper-foil, and boiling, any arsenic is promptly deposited on the copper. The boiling is continued for thirty minutes, any water lost by evaporation being replaced. If the copper has undergone darkening it is dried in the water-oven, cut into strips, and heated in a narrow tube, when a characteristic deposit of arsenious oxide, in the form of microscopic octahedra or tetrahedra, will be obtained if the deposit on the copper was due to arsenic. Unless these crystals can be obtained I am not satisfied that arsenic is present. In doubtful cases, a better definition of the crystals can be obtained by filling the tube with water, which acts only very slowly on crystallised arsenious oxide, and, in my opinion, is preferable to alcohol.

This process has the advantage that the arsenic is actually seen and identified as such. Several such deposits can be united, and the arsenic again deposited on copper or subjected to Marsh's test.

I leave the question of the determination of arsenic in beer for a future communication.

Since the foregoing notes were written the Expert Committee appointed by the Manchester Brewers' Central Association have issued their report. They strongly advocate Reinsch's test, but make no reference to the importance of ensuring that the arsenic is in the arsenious condition. The omission has called from Mr. J. A. Wanklyn a reminder that an "eminent German chemist" (name not stated), in 1861, made an elaborate investigation which showed that 20 grains of arsenic "in one of its commonest forms" (form not stated), dissolved in a gallon of liquid would remain undetected by the method recommended by the experts. One detail in the expert's process is very valuable, and that is the direction to warm the upper part of the sublimation-tube before heating the copper. This precaution results in the deposition of much larger crystals of arsenious oxide than are otherwise obtained.

In the CHEMICAL NEWS of December 21st Messrs. A. Wynter Blyth and H. G. Madan independently recommend the treatment of beer with caustic alkali and aluminium, and utilise the reaction of the evolved hydrogen with silver nitrate as a proof of the presence of arsenic. The method is very simple, but the formation of a black stain or precipitate does not appear so convincing as the formation of crystals.

Sheffield, December 28, 1900.

A BIBLIOGRAPHY OF STEEL WORKS
ANALYSIS.

PART VI.

By HARRY BREARLEY.

(Concluded from p. 295).

SULPHUR (continued).

II. EVOLUTION AS SULPHURETTED HYDROGEN.

II.a. Gravimetric Estimation.—

874. ABEL (C. N., vi., 124).—Dissolve Fe in strong HCl, absorb H_2S in PbA_2 , and convert PbS into and weigh as $PbSO_4$.
875. FORBES (C. N., xvi., 105).—Digest with cold HCl, pass H_2S into ammoniacal $ZnCl_2$, boil with HNO_3 , and precipitate as $BaSO_4$.
876. HAMILTON (C. N., xxi., 147).—Absorb H_2S in KHO, oxidise with chlorine, and add $BaCl_2$. Oxidise residue with aqua regia, and collect the small amount of precipitated $BaSO_4$.
877. REINHARDT (Z. I. S. I., 1885, 650).—Absorb in KHO, oxidise with Br and HCl; or absorb in alkaline PbO , and convert PbS to $PbSO_4$. (Z. C. S., lviii., 1464).— $NaHO$ is used containing a known amount of H_2SO_4 in order to assist the collection of the H_2SO_4 from the iron.
878. DROWN (C. N., xxix., 201).—Absorb H_2S in permanganate. decompose the $KMnO_4$ with HCl, and add $BaCl_2$.
879. PETER (Z. I. S. I., 1885, 618).—As 878; using concentrated $KMnO_4$, and applies the process to ferro-silicon.
880. SCHNEIDER (Z. I. S. I., 1893, ii., 532).—Permanganate the best absorbent for H_2S ; neither the residue nor the solution of the metal contains S. The treatment of ferrous $BaSO_4$ with HCl only makes bad results worse.
881. AUCHY (Z. I. S. I., 1896, ii., 445).—Absorb H_2S in alkaline $KMnO_4$, decompose with HCl and oxalic acid, and precipitate as $BaSO_4$. Determine S in the evolution flask residue.
882. KONINCK (C. N., xxiii., 204).—Collect in $AgNO_3$, digest Ag_2S with Br, remove $AgBr$, and precipitate H_2SO_4 as usual; or absorb in neutral Cd salt and titrate liberated acid with KHO. Later (C. N., lviii., 208), absorbs H_2S in $Hg(CN)_2$ and $AmCl$, so as to avoid washing the $AgBr$.
883. MORRELL (C. N., xxviii., 229).—Pass evolved H_2S into ammoniacal Cd solution; precipitated sulphide dried and weighed.
884. LUTSCHER (Z. I. S. I., 1888, i., 379).—Absorb H_2S in alkaline PbO , boil, and settle the PbS by whirling the graduated tube in a centrifugal machine. Accurate to 0.003 per cent.
885. SCHULTE (C. N., lxxv., 47).—Pass H_2S through heated tube into CdA , add $CuSO_4$, filter off CuS , and ignite to CuO . Both P and As interfere if the solution is passed directly into Cu solutions.
886. CRAIG (C. N., xli., 199 and 272).—Absorb in ammoniacal H_2O_2 , acidify, and add $BaCl_2$. All the S is evolved as H_2S , even from cupriferous and white irons (see 891 and 904).
887. MEINECKE (Z. I. S. I., 1888, ii., 333).—As 886; in a current of H, and absorbs in $H_2O_2 + NaHO$.
888. REIS and WIGGERT (Z. I. S. I., 1891, ii., 325).—Evolve in current of CO_2 , absorb in $AmHO + H_2O_2$, and precipitate with $Ba(NO_3)_2$ from an exactly neutral solution. The precipitate is easily filtered.
889. REIS (Z. I. S. I., 1895, i., 509).—Use HCl of 1.09 sp. gr.; boil to thick fluid, and absorb H_2S in $AmHO + H_2O_2$. H_2O_2 may contain H_2SO_4 or fluo-silicic acid. CO_2 must not be used to carry H_2S forward. By boiling H_2O_2 solution, S may be oxidised beyond H_2SO_4 , difficult to precipitate with $BaCl_2$. All these points are guarded against.
890. SPULLER and KAHLMANN (Z. I. S. I., 1895, i., 512).—Absorb in Na_2O_2 in current of deoxidised air. Decompose Na_2O_2 by boiling and $KMnO_4$. Precipitate as usual.
891. ROCHOLL (C. N., xli., 236).—S may always be found in the residue, particularly when cupriferous irons are assayed.
892. BRUGMAN (C. N., liv., 290).—Copper is no detriment to the evolution process, even when present up to 1 per cent.
893. BRAND (Z. I. S. I., 1884, 660).—Absorb in a burette of glass beads moistened with Br water; precipitate as usual.
894. TROILIUS (Z. I. S. I., 1884, 333).—Absorb in HCl+Br, pour into $BaCl_2$, and boil to drive off Br.
895. BLUM (Z. I. S. I., 1892, ii., 515).—When H_2S is absorbed as in 894, subsequent evaporation is necessary, not because Br interferes with the formation of $BaSO_4$, but in order to destroy oily hydrocarbons.
896. ROLLET (Z. I. S. I., 1880, 359) and GONTIERE (Z. S. C. I., 1896, 830).—The HNO_3 and $BaSO_4$ process is untrustworthy. Heat finely-divided metal, fuel, or slag in H (and CO_2). Collect H_2S in $AgNO_3$ and weigh as Ag_2S or Ag (see 935).
897. PHILLIPS (Z. S. C. I., 1896, 218).—The evolved H_2S is accompanied by organic sulphur compounds (methyl sulphide and mercaptan) not easily oxidised (see 908, &c.); pass through hot tube and absorb, in a capacious bottle, with HCl+Br.
898. TREADWELL (C. N., lxiv., 217).—The insoluble sulphide is heated with Fe in CO_2 , the resulting ferrous sulphide treated with HCl, and the H_2S absorbed in $H_2O_2 + AmHO$. (Z. C. S., lxii., 1375).—Insoluble sulphides are quantitatively converted to H_2S by treatment with Sn and HCl without sulphates being attacked.
899. REED (C. N., lxxii., 299).—Simple apparatus for absorbing H_2S in a small volume of liquid. Apparatus for same purpose by Blum (Z. C. S., lxii., 1376; Z. S. C. I., 1893, 1062), Meade (Z. S. C. I., 1897, 934), and Mackenzie (Z. S. C. I., 1893, 624).

II.b. Volumetric Estimation.—

900. ELLIOT (C. N., xxiii., 61 and 143).—Absorb in $NaHO$, and determine H_2S in the acidified solution by titrating with iodine. The insoluble residue contains traces of S existing as sulphate.
901. PAYNE (C. N., lxvi., 286) and LAUDIS (C. N., lxxv., 218).—As 900. The standard iodine is prepared by adding a known amount of $KMnO_4$ to an acid solution of KI.
902. WILSON (C. N., lxiv., 252).—The iodine is standardised by an actual sample containing a known amount of sulphur.
903. KOPPMAYER (C. N., xxix., 134).—Pass evolved H_2S in a current of H into iodised KI, and titrate the excess of free I with hypo.
904. PETERS (C. N., xxv., 11).—With white irons or steels all the S is not evolved as H_2S in 900, part remains with the residue (see 932).
905. HERTING (C. N., lxxv., 109).—As Morrell (883), but titrate the CdS with iodine. It is unnecessary to expel air from the evolution flask with H or CO_2 .
906. TREADWELL (Z. I. S. I., 1893, i., 408) and CROBAUGH (Z. I. S. I., 1899, ii., 486).—Absorb in ammoniacal $CdCl_2$, acidify, and titrate with iodine.
907. THILL (C. N., lxxxi., 54).—Evolves H_2S into alkaline arsenite, pass acid vapours from evolution flask until As_2S_3 is precipitated, and titrate a filtered fraction of the excess As_2O_3 with iodine.
908. PROST (Z. I. S. I., 1889, i., 390).—Part of the S is present in cast-iron as an insoluble organic sulphur compound.
909. HERTING (Z. I. S. I., 1899, i., 484).—Resumé of gravimetric and volumetric processes. H_2S must

- be passed through a hot tube to decompose accompanying $(\text{CH}_3)_2\text{S}$ compounds.
910. CAMPREDON (C. N., lxxii., 299; and *J. I. S. I.*, 1897, ii., 503).—Evolve H_2S through heated tube along with H and CO_2 into ZnA_2 , and titrate ZnS with iodine. Time, fifteen to thirty minutes.
911. HOOPER (C. N., lxxviii., 191).—Collect H_2S in NaHO , and titrate the alkaline solution with PbNO_3 .
912. HATTENSAUR (*J. S. C. I.*, 1891, 797).—Evolution with HCl gives for Siemens metal results identical with those gotten by 782.
913. BOUCHER (C. N., lxxv., 121).—Absorb in NaHO , add to Fe_2Cl_6 , and titrate FeO formed. Insoluble sulphides are treated with iron under charcoal, and estimated as above.
914. CAMMERER (*J. C. S.*, lxxii., 18 and 278) and HANNS (*J. C. S.*, lxxiv., ii., 461).—Most metallic sulphides react with Fe_2Cl_6 after the manner of 913.
915. WEIL (*J. C. S.*, l., 918).—Pass H_2S from mineral sulphide into AmHO solution of Cu and titrate the excess Cu in aliquot filtrate with SnCl_2 . The addition of Zn promotes the decomposition of the mineral.
916. FRIEDHEIM (*J. C. S.*, lii., 396, 618, and 998).—Process 915 is unreliable, because CuO goes down with the sulphide, and the latter tends to oxidise and redissolve. Weil subsequently absorbs in a mixture of CuSO_4 , NaK tartrate, and NaHO .
917. POPE (*J. C. S.*, lxxii., 123).—S is estimated in Ca_2C by decomposing with H_2O , then adding H_2SO_4 , and absorbing H_2S in PbA_2 .
918. KLOBULOW (C. N., liv., 325).—The presence of nascent H in the evolution flask converts SO_2 into H_2S , and may convert H_2SO_4 —or even S—thereto; therefore add Zn to the dissolving substance.
919. FRIEDMANN (*J. C. S.*, l., 739).—Process 918 is not generally applicable.
920. HERTING (*J. I. S. I.*, 1898, ii., 562).—To powdered blast-furnace slag add N/10 iodine, dilute HCl, and titrate unreacted I with hypo.
921. CRAIG (C. N., lxxiv., 266).—Sulphur exists in blast-furnace slags wholly as CaS , and may be determined as in 886, using purified coal-gas to sweep out, &c. Insoluble sulphides are heated with Zn dust. H_2S evolved and estimated as in 913.
922. EGGERTZ (C. N., lxxviii., 15).—Evolved H_2S colours Ag-Cu plate, which is then compared with standards. The amount of S in iron diminishes with time, at least on the surface.
923. RINMANN (*J. I. S. I.*, 1886, 397 and 1022).—Process 922 can be applied only to grey pig-iron; with white irons the results are very low. Möller says the test is quite untrustworthy.
924. OSMOND (C. N., lvii., 142).—Pass H_2S through a series of bulbs containing equal volumes of standard AgNO_3 . No H_2S passes any bulb until all the Ag is precipitated.
925. WIBORGH (C. N., liv., 158).—Pass H_2S through calico soaked in $\text{Cd}(\text{NO}_3)_2$, and compare colour with permanent standards made in the same way. Air must be driven from the flask prior to evolution of H_2S .
926. COHEN (*J. S. C. I.*, 1890, 16).—A simple form of apparatus for making Wiborgh's test.
927. MORGAN (C. N., lvi., 83).—Absorb H_2S in dilute PbA_2 , and compare colour with a series of standards.
928. ARNOLD and HARDY (C. N., lviii., 41, 59, and 71).—Process 927 gives PbS as a precipitate. Evolve H_2S in the presence of nascent H, collect in NaHO , add acidified PbA_2 , and compare tints. Or pass evolved H_2S through a series of PbA_2 tubes, as in 924, and count the number in which PbS is precipitated. Cu does not interfere.
929. LUCAS (*J. I. S. I.*, 1898, ii., 559).—Evolve H_2S by $\text{HCl} + \text{H}_2\text{SO}_4$ (H_2SO_4 alone gives low results), pass through hot tube into alkaline PbO , and estimate colorimetrically.
930. FUNK (*J. C. S.*, lxx., ii., 274).—Dissolve the zinc in HCl, absorb H_2S in $\text{AmHO} + \text{ZnSO}_4$, add paramidodimethylaniline and Fe_2Cl_6 to the acidified solution, and compare the colour (blue) with standard solutions of H_2S . Can detect 0.0001 per cent sulphur.
931. SCHINDLER (*J. I. S. I.*, 1893, i., 408).—The HCl used should be concentrated in order to evolve all the S as H_2S .
932. WILLIAMS (*J. I. S. I.*, 1893, i., 409).—Less S is left in the residue when hot instead of cold HCl is used. One NaHO tube will absorb all the H_2S .
933. KONINCK (*J. I. S. I.*, 1895, ii., 597).—Add SnCl_2 or Sn to evolution flask along with the metal, to prevent oxidation of the FeO .
934. DONATH (*J. C. S.*, lxxiv., ii., 159).—An HCl solution of SnCl_2 reduces SO_2 to H_2S .
935. HOLLERT (C. N., xlvi., 13).—Heat to redness in a current of oxygen mixed with H and CO_2 ; collect evolved H_2S in AgNO_3 .
936. OTEHA (*J. I. S. I.*, 1898, i., 540).—Powdered coke mixed with Zn or Al and treated with HCl; S, evolved as H_2S , is estimated colorimetrically with CdA_2 .

III. MISCELLANEOUS ITEMS.

937. SCHLOSSBERGER (C. N., iii., 192 and 204).— Am_2MoO_4 in HCl gives a blue colour with H_2S or a metallic sulphide.
938. PRICE (C. N., viii., 285).—Any alkaline melt on the outside of a crucible readily absorbs S from a gas flame. The presence of Mn causes the fused salt to creep.
939. KONINGH (*J. C. S.*, lxxviii., ii., 184).—Sulphur may be oxidised to H_2SO_4 by boiling with KHO and permanganate.
940. MAR (C. N., lxxiii., 256).—Free HCl is favourable to the precipitation of Ba with H_2SO_4 , but it does not eliminate the contamination with alkaline salts, nor does dissolving in H_2SO_4 and diluting entirely, but evaporation of H_2SO_4 solution of BaSO_4 to crystallisation does.
941. BROWNING (C. N., lxxviii., 264).— HNO_3 and aqua regia are favourable to the formation of BaSO_4 , as in 940; the precipitate is more crystalline and is not prevented by citrate, &c.
942. JANNASCH (*J. C. S.*, lxxvi., ii., 60).—Se is separated from H_2SO_4 by boiling with hydroxylamine hydrochloride; Se is precipitated.
943. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—S exists in iron in combination with Mn by preference. On treating with Cu solutions, the sulphur combining with the Cu is equivalent to the Mn present in the steel.
944. SCHEURER-KESTNER (*J. S. C. I.*, 1885, 281).—When Fe_2O_3 and CaSO_4 , MgSO_4 , or PbSO_4 are heated together, SO_3 is given off. Probably ferric sulphate is first formed and then decomposed at a higher temperature (see Jannasch, *J. S. C. I.*, 1889, 820); this does not occur with BaSO_4 .
945. ANON. (C. N., xix., 215).—By heating coke at 300° in a current of air at 2 to 3 atmospheres, all the sulphur is eliminated as SO_2 ; the calorific power of the coke is increased.

Analytical Research on some Essences of Jasmin.—MM. Jeancard and Satie.—To prevent the introduction of impurities into essence of jasmin, the authors use vaseline, unprepared by benjoin or orange-flower, instead of pork or beef fat. The perfume is then extracted in the known manner. The results are given of the analysis of several samples prepared in this manner.—*Bu. Soc. Chim.*, Series 3, vol. xxiii., No. 12.

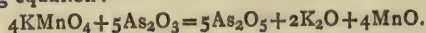
ON THE TITRIMETRIC ESTIMATION OF THE MANGANESE IN MANGANATES BY MEANS OF ALKALINE SOLUTIONS OF ARSENIOUS ACID.

By T. REICHARD.

HAVING undertaken the examination of the manner in which different oxides behave in the presence of arsenious acid, I observed that manganic acid, when submitted to the action of an alkaline solution of arsenious acid, is immediately decomposed, even at the ordinary temperature. In the case of aqueous solutions, even when concentrated, it is necessary to use heat to start the reaction. This becomes manifest at about 50°.

By means of this reaction we are able to use arsenious acid for the estimation of the manganese in manganates, and for determining the oxidising power of these latter.

The decomposition takes place according to the following equation:—



This decomposition of the manganic acid has a double advantage from the analytical point of view. First of all, the arsenious acid, being easy to prepare in a state of perfect purity, can be utilised for the determination of the strength of the manganic acid. Then the manganous oxide set at liberty can be estimated gravimetrically, and thus constitutes a check on the results obtained by the titrimetric method. The indirect volumetric estimation of the manganese in manganates depends on the fact that a solution of arsenious acid of known strength can be compared with a solution of iodine. In a case when an excess of arsenious acid has been used, we can estimate the amount of unconsumed reagent by means of a solution of iodine. A simple calculation then enables us to find the amount of arsenious acid necessary to oxidise the manganic acid. As 5 molecules of arsenious acid are exactly equivalent to 4 atoms of metallic manganese, it is easy to find the amount of this latter body.—*Chemiker Zeitung*, xxiii., p. 801.

THE ESTIMATION OF GLYCERIN.

By CALIXTE FERRIER.

THE glycerin extracted from oils and fats is sold commercially under the name of glycerin from saponification. According to commercial custom it should have a density of 1240, and should not leave more than 5 thousandths of ash or dehydrated incombustible material, after evaporation and calcination of the residue.

The verification of the density depends on methods which are too rigorous to leave any doubt about the results; but the same is not the case with regard to the estimation of the ash.

The results obtained in different commercial laboratories, from the same sample, are rarely concordant, and it is by no means uncommon to meet with differences of 20 or 30 per cent. It is thus evident that the method generally adopted is very defective.

As a rule we proceed in the following manner:—10 grms. of glycerin are evaporated in a platinum crucible, taking as much care as possible to prevent losses by projection. The tarry residue is then burnt in the air, and after extinction of the flame a further residue is left, consisting of carbon mixed with various salts. In order to consume the last traces of the carbon it is necessary to raise the temperature of the crucible to a very high point. The sulphates, chlorides, and alkaline carbonates which are generally found in the residue are melted, and are even volatilised, according to their respective volatilities, if the heating is too violent or too prolonged. It is even

possible for the whole of the alkaline chlorides to disappear before the carbon is entirely burnt away.

When we consider that the temperature is regulated only by the eye of the operator, it is easy to understand how such great divergences in the results are obtained.

It is certainly time to adopt a more trustworthy method, in order to do away with the numerous disagreements which occur. In our laboratory we make use of a method, which is a little longer it is true, but in which we have retained the great simplicity of the old method.

The glycerin is evaporated as has been described above. The tarry residue is burnt, and after roughly crushing the spongy mass which is left after combustion, we pour 5 or 6 c.c. of distilled water into the crucible, allow it to digest for a few moments, and then draw off the clear solution by means of a pipette with a capillary point, which does not allow the fragments of the carbonaceous residue to pass. Such a pipette is easily constructed by drawing out a glass tube in the blowpipe, and cutting off the end at the proper point to obtain a small opening. A second washing is then made in such a manner as not to use more than 10 or 12 c.c. of water altogether; this solution is retained.

The contents of the crucible are then dried and calcined at the temperature necessary for burning off the whole of the carbon. It must be observed that with this residue, from which all the soluble salts have been removed, the calcination is very rapid, and the disappearance of the carbon almost instantaneous.

After cooling, the wash-water is added to the calcined residue, and evaporated with the usual precautions. The crucible is then thoroughly dried, and raised to a red heat for a few seconds over a Bunsen flame.

By this method we have obtained constant results, exact to a ten-thousandth.—*Moniteur Scientifique*, December, 1900, p. 808.

ON THE OCCURRENCE OF TIN IN PRESERVED MEAT, TOGETHER WITH SOME OBSERVATIONS ON THE ESTIMATION OF, AND THE COMPOUNDS OF TIN IN PRESERVED MEAT.

By F. WIRTHLE.

SOME time ago I had occasion to search for tin in several samples of preserved meat, which had for a longer or shorter period (one to five years), been kept in tinned iron boxes. It was necessary at the same time to determine the state of combination of the tin absorbed by the meat, a problem which offered but little chance of success. An examination of the receptacles satisfied me that the layer of tin only contained a very small portion of lead (0.21 per cent); there was no soldered joint. In most cases the meat was separated from the juices containing the greater part of the fat, and these two portions were analysed separately. The results obtained are given in the accompanying table.

It will be seen that the amount of tin increases, as a rule, with the time of preservation, with the exception of the two-year old samples, and this might have been due to the nature of the meat. The quantity of tin is remarkably high in the case of the sample of meat preserved for five years, and the internal surface of the box was completely corroded. The meat absorbed three times as much tin as the juices, a fact similar to that recently observed by Günther (*Chemiker Zeitung*, 1900, xxiv., 50), in a sample of tinned herrings. To try and find the state of combination of the tin absorbed, the boxes were opened by a longitudinal incision, and their contents carefully removed.

I may here state that I observed that the interior of the

Contents of the box.	Length of time preserved. Years.	Number of samples examined.	Tin, per cent.		Remarks.
			Meat.	Juices.	
Beef	1	2	{ Max. 0.0057 Min. 0.0039	{ 0.0015 0.0014	
Goulasch	1	2	{ Max. 0.0051 Min. 0.0037	{ — —	
Beef	2	2	{ Max. 0.0036 Min. 0.0029	{ 0.0016 0.0011	
Filet	2	1	0.0106	—	Box strongly attacked.
Beef	3	1	0.0074	0.0025	
Goulasch	3	1	0.0056	—	Box slightly attacked.
Filet	3	1	0.0079	0.0024	Do.
Beef	4	2	{ Max. 0.0082 Min. 0.0045	{ 0.0028 0.0018	
Goulasch	4	2	{ Max. 0.0094 Min. 0.0061	{ — —	
Beef	5	4	{ Max. 0.0025 Min. 0.0088	{ 0.014 0.0036	Box very strongly corroded.

boxes were corroded almost exclusively in the places in contact with the fat, while they were intact where there was an accumulation of gelatin. In the two boxes in which the meat had been kept for five years, we were able to detect a white crust on the corroded portions. This crust, though insoluble in water, dissolved easily on the addition of a drop of acid. The sulphuric or nitric solution of this white crust reduced corrosive sublimate and ammoniacal nitrate of silver, and gave a strong chlorine reaction; further, the tin was precipitated by sulphuretted hydrogen.

It is thus shown that the crust found in these tins is formed of basic chloride of tin, the formation of which was due to the action of the chloride of sodium present, on the tinned surface. It appears thus that chloride of sodium plays a prominent part in the corrosion of tinned iron boxes by preserved meats, either by direct action of the salt on the tin, or by first forming organic salts of tin, giving with the chloride of sodium basic stannous chloride and an organic salt of sodium. In the case of the four-year old preserved beef, the white crust was not observed, probably because the contents of the box were liquid. On the other hand, the whole of the interior surface of the box was covered with a thin black layer, which it was impossible to remove, giving sulphuretted hydrogen by the action of dilute acids, and probably formed of sulphide of tin. With the beef preserved for three years, the interior of the box was almost intact, and showed only traces of the white crust, which, dissolved in water containing a few drops of hydrochloric acid, and reduced solutions of mercuric chloride. I have not, however, been able to detect the presence of stannous compounds in boxes containing meat preserved for only one and two years.

With regard to the estimation of the tin in preserved meats and the destruction of the organic matter, I first made experiments with a view to oxidising the meat by means of chlorate of potassium and hydrochloric acid, but I did not obtain any good results. Although the residue from the first oxidation, consisting principally of fat, was oxidised a second time, the residuary fat still held notable quantities of tin. I did not think it advisable to use Kjeldahl's method for destroying the organic matter, as recommended by Halenke (*Chemiker Zeitung, Repert.*, 1899, xxiii., 99), because the amount of sample to be taken, viz., 120 grms., requires too large a quantity of sulphuric acid (400 c.c.). I finally adopted Orfila's process, which was recommended by K. B. Lehmann (*Archiv. Hygiene*, 1895, xxiv., 1), a process which I had already found to be of great service for the estimation of copper in preserved peas. The following is the method I finally adopted:—About 120 grms. of meat (the juices, separated from the meat and analysed apart, were treated in the same manner), were placed in a large porcelain dish of nearly 1 litre capacity, moistened with 5 c.c. of concentrated sulphuric acid, and heated carefully on a sheet of asbestos. It was frequently stirred, and from time to time small quantities

of sulphuric acid were added, altogether about 15 to 20 c.c.; the mass was occasionally removed from the sides of the crucible, to which it adhered, by means of a porcelain spatula. We thus obtained, after four or five hours, a porous carbonaceous mass, which was pulverised and incinerated in a porcelain crucible. The particles adhering to the porcelain dish were transferred to the crucible with the assistance of powdered anhydrous carbonate of soda; a further proportion of carbonate of soda was added, together with a sufficient quantity of nitrate of soda, the whole thoroughly mixed, and heated to gentle fusion. After cooling, the melted mass was taken up with water, and the cloudy solution obtained submitted to the action of a current of carbonic anhydride. When the cloudy solution had become quite clear (which generally takes place after about twelve hours), the precipitate was collected on a filter, well washed, dried, and incinerated. The ash was treated with a sufficient quantity of cyanide of potassium, and the mixture heated to dull redness, the crucible being closed. The melted mass was taken up with warm water, and the metallic tin and the iron collected on a filter, washed, and dissolved in a little warm hydrochloric acid. In the solution, which should not be very acid, the tin is precipitated with sulphuretted hydrogen, the precipitated sulphide is washed with water, saturated with sulphuretted hydrogen, and containing a small quantity of nitrate of ammonium, and then dried, incinerated, and calcined until the weight is constant.

The weighed stannic oxide is reduced once more by means of cyanide of potassium; the tin thus obtained is dissolved in hydrochloric acid, precipitated in the form of sulphide, and weighed as stannic oxide. — *Chemiker Zeitung*, 1900, p. 263.

THE ALLOTROPIC FORMS OF SELENIUM.*

By A. P. SAUNDERS.

(Continued from p. 298).

4. Red Crystalline Selenium.

THE methods by which this form may be obtained have been sufficiently illustrated in the description of the behaviour of the amorphous form in solvents. The direct change from the vitreous or amorphous modification to the red crystalline in the absence of solvents, has, as I have stated elsewhere, never been observed with certainty. There is no obvious reason why this change should not go on, and it is quite possible it could actually be observed by bringing the two forms in contact at a moderate heat.

As an exception to the general rule that selenium separates in the amorphous state when set free, it may be noted here that solutions of selenium in carbon disulphide throw down, on the addition of benzene, a shower of

* From the *Journal of Physical Chemistry*, vol. iv., No. 6.

minute glittering plates, of pale red colour; the separation is not instantaneous.

The behaviour of vitreous selenium in carbon disulphide and Rammelsberg's determinations of the solubility of the amorphous form, point to the conclusion that the red crystalline form has, as we would expect, a lower solubility than those others. Exact measurements in this field are still wanting. The crystals which are obtained from carbon disulphide are very beautiful in form and colour, though small. They are readily broken under pressure, and yield a red powder which is indistinguishable from the amorphous modification. The red crystals, which have, in the mass, a dark maroon colour, are quite stable at ordinary temperatures. Mitscherlich, who first obtained and studied them, states that they are stable at 100° , but go over at 150° to the metallic form. Rammelsberg records later that they are instable even at 100° , but Muthmann (1891), who separated two distinct crystalline forms, places the limit of stability for the first, the ordinary form, at 110 — 120° , and for the second at 125 — 130° . The second form is, according to Muthmann, stable at 110° .

No further work has been done upon these two forms, the crystallographic properties of which will be considered below.

If their relationship to liquid selenium on the one hand, and to the metallic form on the other, is what I have supposed it to be, then the red crystals should have an instable melting-point below 217° . Mitscherlich records an observation bearing upon this, to the effect that these red crystals melt if rapidly heated to 200° .

This observation is perfectly easy to repeat, but it does not prove that the crystals have a melting-point at that temperature. We know, from Regnault's observations, that the heat of reaction in passing from the amorphous to the metallic form is large enough to raise the temperature of the selenium about 200° ; but since the red crystalline form is intermediate between these two, it is quite probable that a considerable quantity of heat is evolved when it is carried over to the metallic form; hence this apparently real melting-point may represent only what we may call a case of self-fusion, in which a part of the material in going over to the metallic form raises the temperature of the remainder to its melting-point. When some of the powder of the crystals is dropped on a platinum-plate, heated by means of an oil-bath to 170° or above, the powder melts, and this fusion is followed by an immediate transformation to the metallic form. Below 170° the change goes on more slowly and without fusion. By dropping the powder into a test-tube plunged in the bath, substantially the same results are obtained. Since the crystals are not themselves a form of the liquid modification, it is only necessary to show that, in melting, their temperature does not rise to 217° in order to establish the instable melting-point. For this purpose the powder of the crystals was mixed with some high-melting organic compounds, kindly supplied to me by Dr. C. E. Brewer, in this laboratory. The compounds used are:—Anisic acid, melting-point, 180° ; tri-methyl-acetyl-gallein, 196° ; and gallein acetate, 215° . The corresponding bath temperatures used were 170° , 190° , 205° respectively, and in no case was there evidence of fusion of the organic substance. The best results were obtained at 205° , the fusion of the selenium itself being less complete at the other temperatures; at this point the selenium was completely fused, whereas the crystals of the gallein acetate, although in intimate contact with the selenium, remained unchanged.

This experiment, taken in conjunction with the preceding one, shows that the red crystalline form has probably an instable melting-point at 170 — 180° .

The crystallography of this form of selenium was first studied by Mitscherlich (1855). He noted that selenium separates from carbon disulphide in two different crystal habits: (1) as thin, transparent, red, brilliant leaflets, and (2) as grains which are so intensely coloured as to appear opaque and almost black, although thin fragments of them

show the transparency and colour of the leaflets. He obtained the largest crystals by placing amorphous selenium together with carbon disulphide in a sealed tube, and subjecting this to successive changes of temperature between that of the room and a point somewhat below 100° . The crystals so obtained were scarcely 1 m.m. broad, but had such well-developed faces that it was possible to determine the angles by means of the goniometer.

Mitscherlich finds that the crystals are monoclinic; the better developed ones show a great variety of faces. He made a good many measurements of the angles, for which, however, the original article must be consulted.

Muthmann (1891), was able to separate two monoclinic forms, both obtained from carbon disulphide solutions; and he found that they possessed different degrees of stability. With regard to the form studied by Mitscherlich, Muthmann's results are confirmatory in the main. The axial relationships he found to be—

$$a : b : c = 1.63495 : 1 : 1.6095 \\ \beta = 75^{\circ} 58'.$$

The commonest faces are OP, ∞ P ∞ , +P—P, and ∞ P ∞ , though Muthmann also finds many other faces upon the better developed crystals. The colour is orange-red with a not very pronounced semi-metallic lustre.

The second form appears as short thick prisms with very pronounced semi-metallic lustre; they also are monoclinic, but the axial relationships are different—

$$a : b : c = 1.5916 : 1 : 1.352. \\ \beta = 86^{\circ} 56'.$$

The observed faces were ∞ P, OP, ∞ P ∞ , and P ∞ . This form comes out sometimes as leaflets, which are then easily confused with crystals of the first form. The colour is deep red.

(To be continued).

INAUGURATION OF MEMORIAL BUST OF DR. E. DIVERS.

A LARGE and interesting meeting was held on Saturday, November 17, in the ground of the Tokyo Imperial University, to inaugurate the memorial bust of Dr. Edward Divers, erected by his friends and former pupils, in front of the Science College, in grateful remembrance of his long and important services in Japan. Past and present Presidents of the University, most of the Professors, and a large number of Dr. Divers' former pupils attended the meeting, whilst Mr. E. W. Tilden, son-in-law of Dr. Divers, came up from Kobe specially for the occasion.

The ceremony was opened at 11.30 a.m. by an address by Prof. J. SAKURAI, who represented the Committee, and who dwelt, at some length, upon the important services done by Dr. Divers, both in the former Engineering College and the present Science College, during the past quarter of a century, and both in the capacity of a teacher and that of an investigator. The bust was then unveiled amidst loud cheers, and presented to the University.

Dr. D. KIKUCHI, President of the University, next read an address, in which he referred to the high recognition by the University of the important works done by Dr. Divers for the cause of education and science, and expressed the pleasure, in his official capacity, of accepting the bust.

Mr. E. W. TILDEN, on behalf of Dr. Divers and his family, briefly thanked for the courteous way in which the Doctor's friends and former pupils expressed their appreciation of his services.

The ceremony was concluded by a speech by Mr. H. WATANABE, one of the oldest friends of Dr. Divers, and who referred to his official connections with the learned Doctor both at the old Kobudaigakko and the Imperial University, and expressed his admiration of the long and unwearied work of Dr. Divers.

Music was played by the Tokyo City Band between the addresses and speeches, and afterwards refreshments were served at Dr. Divers' former residence.

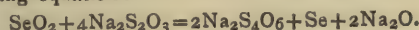
The bust, which was executed by Mr. Naganuma, won an unanimous approbation.

THE REDUCTION OF SELENIUM DIOXIDE BY SODIUM THIOSULPHATE.

By JAMES F. NORRIS and HENRY FAY.

SOME time ago we proposed a volumetric method for the estimation of selenous acid (*Amer. Chem. Journ.*, xviii., 703) based on the reaction between it and sodium thiosulphate in the presence of hydrochloric acid. The procedure, in brief, is as follows:—The solution in which the selenous acid is to be determined is diluted with ice-water, acidified with dilute hydrochloric acid, and an excess of a tenth-normal solution of sodium thiosulphate added. The excess of thiosulphate is determined by titration with a solution of iodine. It was shown that 1 molecule of selenous acid reacted with 4 molecules of sodium thiosulphate, and that the reaction afforded a means for the accurate determination of selenium.

At the time this method was proposed we were not able to state the exact nature of the reaction, but we have studied further the reduction, and are now able to write the complete reaction. The most probable reaction between the two substances may be represented by the following equation:—

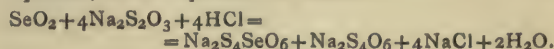


If strong solutions of selenium dioxide and sodium thiosulphate are mixed, selenium is precipitated, and the solution shows an alkaline reaction. In dilute solutions, on the other hand, no selenium is precipitated, and the reaction is not complete according to the above equation, since the sodium hydroxide formed neutralises a part of the selenous acid which, accordingly, does not enter into the reaction. If, however, acid is present, 4 molecules of sodium thiosulphate react with 1 molecule of selenium dioxide. The amount of acid required to complete the reaction was determined. This was found to vary with the dilution, the excess of thiosulphate, and the time of reaction. The following table gives the results obtained. In each case 10 c.c. of a solution of selenium dioxide, which was equivalent to 26.40 c.c. of sodium thiosulphate, according to the ratio $\text{SeO}_2 : 4\text{Na}_2\text{S}_2\text{O}_3$, were used.

	Molecules HCl.	$\text{Na}_2\text{S}_2\text{O}_3$ taken. C.c.	$\text{Na}_2\text{S}_4\text{O}_6$ used. C.c.	Water added. C.c.
I.	3	50	17.90	—
II.	4	27	22.02	300
III.	4	27	24.96	300
IV.	4	50	25.40	300
V.	5	30	26.38	300
VI.	4	50	26.40	—

In Experiment I., 3 molecules of acid were used, and only 17.90 c.c. of thiosulphate entered into the reaction. Using 4 molecules in II., 22.02 c.c. of thiosulphate reacted. In the third experiment the same proportions were used, but the solutions stood forty minutes before the excess was determined. This had a marked effect on the result, as about 3 c.c. more of the thiosulphate reacted. A large excess of thiosulphate hastened the reaction, as is shown in Experiment IV. Experiment V. shows that 5 molecules of acid are sufficient at a dilution of 300 c.c., and with a slight excess of sodium thiosulphate, to complete the reaction. In Experiment VI. no water was added to the solutions used, and the reaction was complete when the proportion of the reagents were $\text{SeO}_2 : 4\text{Na}_2\text{S}_2\text{O}_3 : 4\text{HCl}$. These are, therefore, the amounts of reagents which enter into the reaction.

In order to determine the products of the reaction, a solution of the constituents in the above proportions was prepared. The study of this solution led to the following equation, which expresses the reaction:—



The formation of sodium selenopentathionate, similar to potassium pentathionate, seemed probable, since no selenium was precipitated as a result of the reduction. Debus (*Journ. Chem. Soc.*, liii., 278), in an exhaustive study of Wackenroder's solution, which is prepared by the action of hydrogen sulphide on an aqueous solution of sulphur dioxide, isolated some salts of pentathionic acid in a pure condition, and carefully studied their properties. He gives the following characteristic reactions:—

"I. An ammoniacal solution of silver nitrate causes, in a solution of potassic, ammoniac, or baric pentathionates, a brown colouration which rapidly becomes darker, and by degrees a black precipitate is thrown down from the mixture. This reaction is not produced in a solution of tri- or tetrathionates, potassic thiosulphate, or ammoniac sulphite. An ammoniacal solution of silver nitrate also seems to have no effect on them. Consequently a pentathionate, even if present in very small quantity, can be detected by means of this reaction in a mixture containing potassic tri- and tetrathionates, and sodic, potassic, or ammoniac thiosulphates.

"II. Potassic hydroxide, in solutions of pentathionates, immediately produces a separation of sulphur. Astri- and tetrathionates and thiosulphates are not changed by this reagent, a proportionally small quantity of a pentathionate can be detected in a mixture of the four salts by addition of potassic hydroxide.

"III. Ammonia added to a solution of potassic pentathionate causes, after about one or two minutes, a precipitation of sulphur.

"IV. Hydric chloride does not change solutions of tetra- and pentathionates."

A solution prepared by mixing the constituents in the proportions represented in the equation was subjected to the above tests. A precipitate was formed with ammoniacal silver nitrate, as described above under I., and potassium hydroxide caused an immediate precipitation of selenium. Ammonia acted more slowly, and the solution was stable toward strong hydrochloric acid. The solution showed, therefore, the characteristic reactions of a pentathionate, selenium, however, being precipitated instead of sulphur. This is in accord with the formula proposed, $\text{Na}_2\text{S}_4\text{SeO}_6$. An effort was made to isolate the selenopentathionate, but without success, as selenium was always precipitated when the solutions were concentrated by heat or in a vacuum. From the solution, however, we were able to isolate sodium tetrathionate, which was proved to be such by qualitative and quantitative analysis.

A dilute solution containing the new salt could be boiled some time without change. A number of neutral salts were found to decompose the compound. Stannous chloride caused a precipitation of selenium after a few minutes. A dilute solution of sodium thiosulphate produced the same effect, only much more slowly, whereas a number of hours' standing was necessary before potassium iodide caused any decomposition.

An acid solution of tellurium dioxide is reduced by sodium thiosulphate, giving a bright yellow solution, from which sodium hydroxide precipitates tellurium. Tellurium, therefore, probably forms a compound analogous to a selenopentathionate. This is remarkable, since no compounds containing tellurium, analogous to the thionates, are known. Crane (Johns Hopkins University) attempted to prepare substances similar to the thiosulphates, by boiling sodium tellurite with sulphur, selenium, and tellurium, but there was apparently no reaction.

By misunderstanding a statement made in our former paper, Mr. J. T. Norton, Jun. (*Amer. Journ. Sci.*, clxvii., 287), has been led to study the influence of hydrochloric

acid on titrations with sodium thiosulphate, and to repeat our work on the estimation of selenium. He says, referring to the method, "the explicit statement of the authors that the amount of hydrochloric acid present does not influence the result provided the titration is made at the temperature of melting ice, is so extraordinary in view of generally accepted ideas in regard to the interaction of hydrochloric acid and sodium thiosulphate, as to suggest the necessity of a careful investigation of this point." In the paper referred to we made this statement:—"It was found necessary to have enough hydrochloric acid present to set free all of the thiosulphuric acid. If the solution is cold a large excess of hydrochloric acid does not affect the titration." Mr. Norton evidently confuses *excess* with *amount*. We used in all of our experiments 10 c.c. hydrochloric acid (1·12 sp. gr.), which is seven to eight times the amount required according to the above statement, and obtained excellent results. The statement is, therefore, not so extraordinary as might appear.

As the action of hydrochloric acid on sodium thiosulphate was known to us when we were making a study of the method, we took the precautions to have the solutions containing the acid dilute, and used ice to keep the temperature as low as possible. The necessity for these precautions was stated in the directions given, Mr. Norton further points out that it is advisable to use not more than 20 c.c. excess of sodium thiosulphate in order to prevent decomposition by the acid. We have made some new determinations of selenium in order to test the directions given in the original paper under the most unfavourable conditions. The results follow:—

	SeO ₂ taken. Grm.	Na ₂ S ₂ O ₃ taken. C.c.	Na ₂ S ₂ O ₃ used in reaction. C.c.	SeO ₂ found. Grm.	Dilution. C.c.
I.	0·0995	43	39·62	0·0995	300
II.	0·0336	15	13·39	0·0336	300
III.	0·0336	50	13·13	0·0331	300
IV.	0·0336	50	13·24	0·0333	300
V.	0·0435	50	17·20	0·0432	400
VI.	0·0430	50	16·41	0·0412	200

In Experiments I. and II. the directions as given in our paper were followed, and a small excess of sodium thiosulphate was used. In order to have a large excess of thiosulphate present in the other experiments, small amounts of selenium dioxide and 50 c.c. of thiosulphate were used. In III. and IV. the excess, 36·87 c.c., was nearly three times the amount necessary for the reaction—13·13 c.c. Since a bare excess only is necessary, a careful analysis would hardly be based on such a procedure. Experiment VI. shows the necessity of working in dilute solutions. In all of the above determinations 10 c.c. hydrochloric acid (1·12 sp. gr.) were used, but since 5 c.c. is quite sufficient to bring about the reaction, the modification which Mr. Norton suggests as the result of his work, namely, the use of the latter amount of acid, can readily be accepted.

Mr. Norton points out also that his results always come high. We had not observed this in our work, and accordingly we sought the cause. As we had standardised the sodium thiosulphate by titration against known weights of iodine, under the conditions which were to be used in the subsequent analyses—that is, titration in the cold in the presence of acid—a standardisation was made under ordinary conditions. The factor found was higher by about 0·2 per cent than the one previously obtained. This discrepancy was shown to be due to the fact that the iodine-starch reaction is more sensitive at 3° in presence of dilute acids than under the conditions which are ordinarily used in the titration of iodine and thiosulphate. The following table gives the number of cubic centimetres of one-hundredth normal iodine solution required to produce a colour with starch under different conditions of temperature and with varying amounts of dilute hydrochloric acid (sp. gr. 1·12). The starch solution was made by grinding 2 grms. of soluble starch with 5 c.c. of cold

water, and pouring the mixture into 500 c.c. boiling water. In all tests 5 c.c. of this solution were used and diluted to 300 c.c. with water.

No.	Acid. C.c.	Temperature.	Iodine.
1	—	20°	0·61
2	1·00	20°	0·32
3	10·00	20°	0·26
4	50·00	20°	0·27
5	—	3°	0·30
6	—	15°	0·50
7	—	20°	0·57
8	—	25°	0·85
9	—	30°	1·17
10	10·00	3°	0·15

Experiments 1 to 4 show the effect of acids and 5 to 9 the effect of temperature. In Experiment 10 the most favourable conditions for the reaction were combined and 0·15 c.c. of the iodine solution gave a distinct colour, whereas in the absence of acid, at 25°, 0·85 c.c. was necessary. It has long been known that temperature has an effect on the blue compound formed by the action of iodine on starch, but, as far as we can find, it has never been shown that this effect is appreciable at the temperatures used in the course of an analysis. Although the error arising is small when the facts brought out by the above experiments are overlooked, nevertheless, when very accurate results are desired, they should be taken into consideration.—*American Chemical Journal*, xxiii., No. 2.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

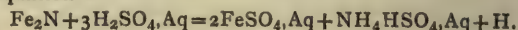
Ordinary Meeting, December 6th, 1900.

Professor THORPE, C.B., F.R.S., President, in the Chair.

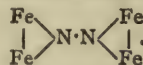
(Concluded from page 300).

162. "The Heat of Formation and Constitution of Iron Nitride." By GILBERT JOHN FOWLER, M.Sc., and PHILIP J. HARTOG, B.Sc.

To determine the heat of formation of iron nitride, the substance was dissolved in dilute sulphuric acid (containing 49 grms. to the litre), as represented by the equation—



A current of nitrogen was passed through the solution to avoid oxidation of the ferrous salt, as the reaction is a slow one, though it eventually becomes complete. The mean of three determinations gave as the thermal value of the reaction +81·56 cal. From this value the heat of formation of iron nitride is calculated to be +3·04 cal. It is suggested that the constitution of iron nitride is—



163. "Infracampholenic Acid: an Isomeric of Campholytic and Isolauronic Acids." By M. O. FORSTER.

By hydrolysing the unsaturated nitrile formed when the anhydride of bromonitrocamphane is treated with hot aqueous sodium hydroxide (*Trans.*, 1899, lxxv., 1141), *infracampholenic acid*, C₉H₁₄O₂, is obtained as a viscous oil boiling at 145° and 239°, under pressures of 24 m.m. and 758 m.m. respectively; it is optically inactive, and is transformed into isolauronic acid by hot, dilute, sulphuric acid. The *dibromide*, C₉H₁₄O₂Br₂, produced when a cold solution of bromine (1 mol.) is added to the acid dissolved in chloroform and surrounded by a freezing mixture, crystallises from warm petroleum in minute white needles, which melt at 125° to a colourless liquid

which evolves gas. Tribromodihydroinfracampholenic acid, $C_8H_{13}O_2Br_3$, obtained when infracampholenic acid is submitted to the action of bromine under the conditions which lead to the conversion of campholytic acid into its dibromide, crystallises from ethyl acetate, and melts at 182° to a colourless liquid which evolves gas.

Aminoinfracampholene, $C_8H_{13}NH_2$, prepared from the amide of infracampholenic acid by the action of sodium hypobromite, is a colourless oil which boils at $158-160^\circ$ under 754 m.m. pressure, and has a sp. gr. 0.8770 at 14° . The hydrochloride melts at 213° , the platinichloride at $238-240^\circ$, and the picrate at 213 ; the benzoyl, carbamide, and phenylcarbamide derivatives melt at 105° , 182° , and 180° respectively.

164. "Tutu." Part I. By THOMAS HILL EASTERFIELD and BERNARD CRACROFT ASTON.

The authors have examined three varieties of tutu—*Coriaria ruscifolia*, *C. thymifolia*, *C. angustissima*—which cause serious loss of stock in New Zealand, and have isolated from them a glucoside, tutin, $C_{17}H_{20}O_7$, along with acetic, gallic, succinic, and other acids. From *C. thymifolia* quercetin or an isomeric compound was obtained; and from *C. angustissima* a volatile acid, $C_8H_8O_4$, which has not been identified.

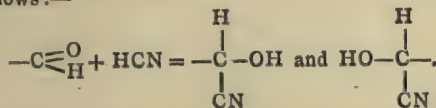
Tutin was obtained in colourless crystals melting at $208-209^\circ$ (uncorr.), and is perceptibly volatile at $120-130^\circ$. Its solubility is 1.9 grms. in 100 grms. water at 10° ; 1.5 grms. in 100 grms. ether at 10° ; 8.2 grms. in 100 grms. alcohol at 16° . It is very soluble in acetone, sparingly soluble in chloroform, insoluble in benzene and carbon disulphide. Its optical rotation was determined, and gives $[\alpha]_{D19} = +9.25^\circ$.

The authors also discussed the formula for coriamyrtin, and conclude that the formula, $C_{15}H_{18}O_5$, which is half that usually accepted, harmonises better with the facts. A comparison of the chemical and physical characters of tutin and coriamyrtin proved that these substances are not identical.

A note by Professor Marshall on the pharmacology of tutin states that its action is similar to that of coriamyrtin, but is more slowly produced, and it is much less toxic. Its action is exerted mainly on the medulla oblongata and the basal ganglia of the brain.

165. "Experiments on the Production of Optically-active Compounds from Inactive Substances." Preliminary Notice. By J. B. COHEN and C. E. WHITELEY.

E. Fischer has shown (*Annalen*, 1892, cclxx., 64) that in the synthesis of one sugar from another by the addition of hydrocyanic acid to the lower member, a new asymmetric carbon atom is introduced, which may give rise to two stereoisomeric compounds. This may be represented as follows:—

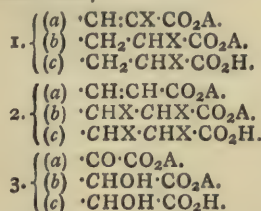


Although the two new groups are optical antipodes, the two isomerides are not necessarily so as a whole, and consequently they are not always produced in equal quantities. Fischer has found, for example, that glucose forms two cyanhydrins in very unequal quantities, whilst in the case of dextro-mannose only one of the two possible cyanhydrins is produced (Hartmann, *Annalen*, 1892, cclxxii., 190). It is clear, therefore, that the asymmetric molecule as a whole exerts its influence on the space configuration of the newly-added asymmetric carbon group. In these examples, it is impossible to determine exactly the influence of the active part of the original molecule on the activity of the new group, seeing that the latter cannot be detached from the molecule. As the formation of active substances in living organisms is probably closely connected with their production from other active substances, from which they are afterwards removed, the idea occurred to us to attempt to produce a new asym-

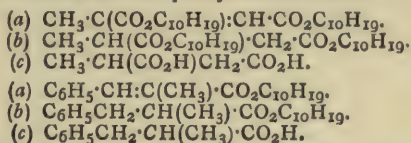
metric carbon atom in an already active compound from which the originally active group could be subsequently detached.

A number of reactions readily presented themselves, such as the reduction, bromination, or hydroxylation of esters composed of an unsaturated acid and an active alcohol, or the reduction of a ketonic ester of an active alcohol, the alcohol being afterwards removed by hydrolysis.

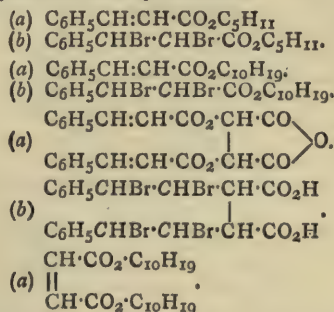
These reactions may be represented as follows: (X stands for an atom or group not being hydrogen, A indicates the active alkyl or aryl group, and C the new asymmetric carbon atom):—



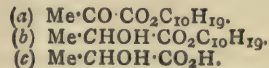
Under (1) we have studied the reduction of the menthyl esters of mesaconic and phenylcrotonic acids.



Under (2) we have prepared the bromine derivatives of the amyl and menthyl esters of cinnamic acid and of dicinnamyl tartrate, and examined the action of various reagents on the dibromo-compounds, also the action of sodium ethylate on menthyl fumarate.



Under (3) we have investigated the reduction of menthyl pyruvate.



The results in all cases have been of a negative character, in spite of every care to avoid possible racemisation by conducting the reactions as far as possible at the ordinary temperature.

The experiments, which were commenced in 1898, have been delayed in consequence of unforeseen difficulties. All the experiments under (2), after a considerable loss of time, had to be abandoned. Although the dibromoderivatives of amyl and menthyl cinnamate and of dicinnamyl tartrate could be readily obtained in a state of purity, they could not be directly hydrolysed without removing bromine, and all attempts to replace the bromine by hydroxyl failed. Menthyl fumarate, which was readily prepared from silver fumarate and menthyl chloride, gave no ethoxy-derivative by means of Purdie's reaction. Reactions (1) and (3) were, however, ultimately brought to a satisfactory conclusion.

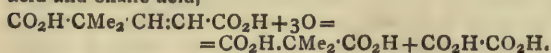
Menthyl mesconate and menthyl phenylcrotonate were

prepared by heating together menthol and the acid chloride, whilst menthyl pyruvate was obtained by heating menthol and pyruvic acid under diminished pressure. The reduction of the first two esters was effected by means of the aluminium-mercury couple in aqueous alcoholic solution, whilst menthyl pyruvate was reduced with zinc dust and acetic acid. The esters were then hydrolysed with alcoholic potash and the menthol removed with ether. The acid, after careful purification by crystallisation or precipitation of its salt, was finally examined in the polarimeter. Pyrotartaric acid, phenylmethylacetic acid, and lactic acid, obtained in this way, were all optically inactive. We propose to extend these experiments to the acid amides of optically active bases.

166. "Synthesis of Isocamphoronic Acid." By W. H. PERKIN, Jun.

When the anhydride of $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, *aa*-dimethylglutaric acid, is treated with phosphorus pentachloride and bromine, and the product poured into alcohol, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$, *ethylbromodimethylglutarate* is obtained as a colourless oil boiling at $165-170^\circ$ (35 m.m.).

This, on treatment with alcoholic potash, yields *dimethylglutaconic acid*, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, which crystallises from water in plates melting at 172° , and is possibly a stereoisomeride of the *aa*-dimethylglutaconic acid lately prepared by M. Conrad (*Ber.*, 1900, xxxiii, 1920), which melts at 150° . That the acid of melting-point 172° has the constitution assigned to it is proved by the fact that when oxidised with permanganate at 0° it is quantitatively converted into dimethylmalonic acid and oxalic acid,—



Dimethylglutaconic acid is readily esterified by means of alcohol and sulphuric acid: the *ethyldimethylglutaconate*, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$, thus produced, is a colourless oil boiling at 200° (200 m.m.).

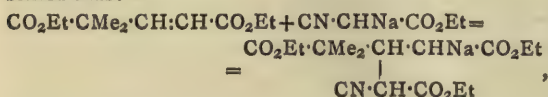
When this ester is digested in alcoholic solution with the sodium compound of cyanacetic ester, condensation takes place, and the product, on heating with dilute sulphuric acid, is almost quantitatively converted into an acid melting at 166° , and which on examination has been proved to be *isocamphoronic acid*.

(Found: C=49.7; H=6.5; $\text{C}_9\text{H}_{14}\text{O}_6$ requires C=49.5; H=6.4).

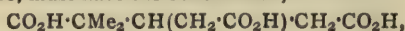
Professor von Baeyer was kind enough to send the author a sample of isocamphoronic acid which had been prepared from pinene, and on mixing equal quantities of this and the synthetical acid no alteration in the melting-point could be observed. Again, when heated with sulphuric acid at 100° , the synthetical acid is converted into *terpenylic acid*, a change which Tiemann (*Ber.*, 1896, xxix, 2613) has shown to be characteristic of isocamphoronic acid.

There can thus be no doubt that the synthetical acid is in reality isocamphoronic acid, and its synthesis solves the vexed question of the constitution of this important acid.

The condensation of ethyl dimethylglutaconate with the sodium compound of ethyl cyanacetate may be represented thus:—



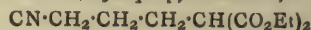
and the cyanester thus produced yields, on hydrolysis and elimination of carbon dioxide, isocamphoronic acid, which, therefore, must have the constitution,—



first proposed for this acid by Tiemann (*Ber.*, 1896, xxix, 2614).

167. "On some α -Alkyl Substitution Products of Glutaric, Adipic, and Pimelic Acids." By J. W. MELLOR.

The author describes the known methods of general application for the preparation of the above acids, and gives an account of some new methods which he has employed in synthesising such acids. He finds that adipic acid itself may be readily prepared in quantity by the action of *chloropropylcyanide*, $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$, on the sodium compound of ethyl malonate, and subsequent hydrolysis of the *ethylanpropylmalonate*,—



(b.p. $170-175^\circ$ at 40 m.m.), by boiling with dilute sulphuric acid. α -Alkyl substitution products of adipic acid may be obtained by employing the corresponding ethyl α -alkyl malonates in this synthesis in the place of ethyl malonate.

The author has prepared several of the known α -alkyl substitution products of glutaric, adipic, and pimelic acids in a state of purity, and determined their dissociation constants. He has also prepared *α -propyl adipic acid*, $\text{CO}_2\text{H}\cdot\text{CHPr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which melts at 59° , and does not appear to have been previously described.

168. "On the Nature of Polyiodides and their Dissociation in Aqueous Solutions." By H. M. DAWSON.

From experiments on the ratio of distribution of iodine between solutions of potassium iodide and carbon bisulphide, and the simplicity of the dissociation isotherm for the equilibrium in the aqueous solution, which accords with the experimental data, it is concluded that potassium triiodide is a normal salt of potassium, which at corresponding concentrations is dissociated electrolytically to the same extent as other binary salts. Experiments with solutions of hydriodic acid lead to the conclusion that hydrogen triiodide is electrolytically dissociated to the same extent as hydriodic acid, and belongs, therefore, to the group of strong acids. These results are in harmony with Abegg and Bodländer's theory of complex compounds. From their analogy with potassium triiodide, the recently discovered trihaloid derivatives of caesium and rubidium must be placed in the same category.

NOTICES OF BOOKS.

A Manual of Assaying: the Fire Assay of Gold, Silver, and Lead, including Amalgamation and Chlorination Tests. By ALFRED STANLEY MILLER. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1900. 87 pp. 12 mo. Illustrated.

In the Preface to this little volume the author explains that it departs from the plans of other books, by introducing the apparatus where its use is easily understood. "The student is taught the operations of the fire-assay by practising with an ore easy to assay; he is then better prepared to understand the directions for assaying more complex ores." In the first chapter the student is told how to make cupels and flux; in the second, how to prepare a sample of ore, and how to make an assay of a siliceous gold and silver ore.

The instructions are clear, and the many illustrations aid in their comprehension. The author cites standard works on the subject. There is an index.

H.C.B.

Chemistry for Examinations. By HENRY W. HILL. London: Allman and Son. 1900. Pp. 130.

As examinations are a necessary evil, it follows that books will be published with the sole object of helping the idle student to "cram"; a diligent man has no need for such artificial help.

The book now before us has been written more particularly to meet the requirements of the Oxford and Cambridge Local Examinations; and we further notice that, so as to prevent younger men overloading their minds, all sections

which are of importance to senior students only have been marked with an asterisk.

Considering its avowed object, this volume is well planned, and covers a fairly wide range of elementary theoretical chemistry. It also contains a "Special Part" which includes sections devoted to chemical diagrams and equations, and to several original tables, notably comprehensive tables of colour and solubility.

CORRESPONDENCE.

DETECTION OF ARSENIC.

To the Editor of the Chemical News.

SIR,—The difficulty that Mr. Estcourt experienced when trying to detect arsenic in Manchester beer without previous treatment by means of Marsh's test, is one that is likely to occur when any substance containing sulphites and sulphides, or any other compound that contains sulphur that is converted into sulphuretted hydrogen by zinc and acid, is examined by means of Marsh's test for arsenic.

The reason of this was pointed out indirectly by Otto Fehr and der Pfordten in a paper on the "Removal of Arsenic from Sulphuretted Hydrogen," published in the *Ber.*, xvii., 2897, and abstracted in the *Journal of the Society of Chemical Industry* for 1885, and no doubt in other journals and papers. The reactions bearing on the above subject mentioned by him are as follows:—

The decomposition of sulphuretted hydrogen at temperatures from 350° to 400° C. The decomposition of arsenuretted hydrogen at higher temperatures, and the mutual reaction of arsenic in sulphuretted hydrogen between 350° and 360° C., which reaction he says is not complete at this temperature.

I have no doubt that if Mr. Estcourt analyses the substance he obtained in heated tubes he will find that it was a mixture of free sulphur and sulphide of arsenic, which I have frequently got when testing similar mixtures.—I am, &c.,

JAS. F. SMITH.

30, Chester Road, Akroydon, Halifax.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 23, December 3, 1900.

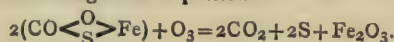
Samarium Carbide.—Henri Moissan. —Samarium oxide, at the temperature of the electric furnace and in presence of carbon, forms a crystallised carbide of formula SaC_2 . The composition of this carbide is comparable with that of the carbides of cerium, lanthanum, neodymium, and praseodymium. It decomposes cold water in the same way as the carbides of the alkaline earths, giving a complex mixture of hydrocarbons very rich in acetylene. It has a density of 5.86, a yellow colour, and, when examined under the microscope, has a crystalline appearance—the particles having an hexagonal shape. This substance burns brilliantly at 400° in a current of oxygen. The decomposition of water by the carbide brings the metal samarium nearer to the yttrium group, and removes it further from the rare earths belonging to the cerium group.

Acidimetry of Aldehydes and Acetones.—A. Astruc and H. Murco.—M. Astruc has already examined the

alkalimetry and acidimetry of the amines, phenols, and organic acids. The authors now examine the reactions furnished by aldehydes and acetones in presence of the colour reagents—helianthine, phenolphthalein, and Poirrier's blue. The following substances were examined:—Monoaldehydes of simple function, dialdehydes of simple function, halogen aldehydes, alcohol and phenol aldehydes, monoacetones of simple function, diacetones, halogen acetones, alcohol acetones, and acid acetones. The authors propose to confirm and extend their researches relative to the aldehydes and acetones by the thermochemical examination of these bodies, which is as yet very incomplete.

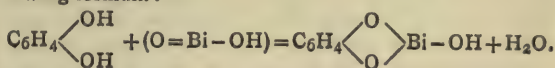
Some Reactions of Substituted Anilines.—Echsner de Coninck.—The author's experiments were performed on extremely pure specimens of methyl, dimethyl, ethyl, and diethyl anilines. The reactions of these substances were noticed with cupric chloride solution, copper sulphate solution, and copper acetate solution, dilute solution of cobalt chloride, dilute solution of nickel chloride, and both these solutions when concentrated. A careful investigation of all these reactions gives a means of identifying and distinguishing the various anilines, but the reactions are apparently masked by impurities.

Presence of Oxysulphocarbonate of Iron in the Water of the Rhone.—H. Causse.—Rhone water, during a period of three months commencing in June, contains iron oxysulphocarbonate. The proportion of this compound, very slight at first, increases progressively until the middle of September, then decreases and disappears in the autumn. The origin of this oxysulphocarbonate of iron may possibly be due to the combination of carbon dioxide with the ferrous sulphide due to the reduction of sulphates by certain organic matters in the river, according to the equation $\text{CO}_2 + \text{FeS} = \text{CO} < \text{O} > \text{Fe}$. In contact with air, this compound appears to be destroyed by the oxygen, according to the equation—



Journal de Pharmacie et de Chimie,
Series 6, Vol. xii., No. 4.

Some Bismutho-Phenolic Compounds.—E. Richard.—A diatomic phenol, such as $\text{C}_6\text{H}_4(\text{OH})_2$, combines with the hydrate of bismuthyl, and gives, owing to the loss of a molecule of water, a compound answering to the following formula:—



For such a reaction to take place it is first necessary for the phenol to have at least two oxyhydriles; another no less important condition is that these two oxyhydriles must be opposite one another in the ortho-position. To prepare these compounds, it is sufficient to add a solution of a bismuth compound to a solution of phenol. For instance, if we add to a slightly warmed solution of pyrocatechin a solution containing an equal weight of bismuth emetic, the solution will first take a yellow colour, then become cloudy, and finally give an abundant deposit of a citron-yellow colour, which is shown by analysis to correspond with the rough formula $\text{C}_6\text{H}_2\text{O}_3 = \text{Bi}$, and which is, in fact, the pyrocatechin hydrate of bismuthyl, $\text{C}_6\text{H}_4\text{O}_2 = \text{Bi} - \text{OH}$, insoluble in water, alcohol, and chloroform. It is decomposed by sulphuric acid, giving sulphate of bismuth; the pyrocatechin is set free, and can be separated with ether. It is decomposed with violence by nitric acid. If, instead of using pyrocatechin, we use resorcin or hydroquinone, no similar reaction takes place, but, on the other hand, this easily occurs if the other diphenols with two oxyhydriles in ortho are used. Gallic acid and gallate of methyl also form a compound with bismuth under the same conditions.

Diphenylcarbazide, a very Sensitive Reagent for some Metallic Compounds (Copper, Mercury, Iron, Chromic Acid).—P. Cazeneuve.—Already noticed.

No. 5.

This number contains no matter of chemical interest.

No. 6.

Analysis of the Waters from the Hot Springs at Djebel Achkel.—M. Puaux.—Already inserted in full.

The Presence of Zinc in Certain Alcohols.—Th. Roman and G. Delluc.—The residue from the evaporation of 1 litre of alcohol at 95° was treated with water, slightly acidulated with acetic acid, and the whole boiled to facilitate the solution and drive off the excess of acid. After filtering, soda gave a white precipitate soluble in excess, carbonate of potassium a white precipitate insoluble in excess, sulphhydrate of ammonia a white precipitate, and ferricyanide a flesh coloured precipitate. The precipitate obtained with carbonate of potassium left, on calcination, a residue which was yellow when hot and white when cold. The presence of zinc is no doubt due to the nature of the vessels in which the alcohol was kept: this was proved by leaving some scrapings from a galvanised iron drum in contact with alcohol at 95° for two days, with frequent agitation, when the presence of zinc in solution was detected; after four days' contact the indications were very strong. The zinc was detected by the addition of urobiline, which gives a greenish fluorescence: this substance is best added in the form of a chloroformic solution of urobiline, which is easily prepared.

Glycerophosphate of Quinine.—M. Prunier.—This substance is best prepared in the following manner:—A saturated solution of glycerophosphate of lime is gradually added to a solution of oxalic acid at about one-twentieth, and carefully stirred, a slight excess of the glycerophosphate must be finally added; this is left for some hours before filtering, so as to precipitate the whole of the oxalic acid. To the clear filtrate a slight excess of hydrate of quinine, suspended in water, is gradually added; this is left until it gives an alkaline reaction with litmus. After saturation in the cold, the whole is brought to boiling to dissolve the salt, and to separate the excess of insoluble quinine by hot filtration. On cooling, an abundant crop of crystals of basic glycerophosphate of quinine is obtained. Under these conditions the salt contains 5 molecules of water, which it gradually loses when the temperature is raised; above 60° it turns brown, and commences to decompose. Its composition is shown to be—Quinine 70 parts, glycerophosphoric acid 19 parts, water 11 parts.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 1st. { Royal Institution, S. (Christmas Lectures to
THURSDAY, " 3rd. { Young People). "On Great Chapters from
SATURDAY, " 5th. { the Book of Nature," by Sir Robert Stawell
Ball, D.Sc., LL.D., F.R.S.

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